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### Studies Towards the Living Polymerisation of Phenylethynyl-calix[4]arene Compounds with Rh-based Ternary Catalytic Systems

Alexandra I. Costa<sup>a</sup>; José V. Prata<sup>a</sup>

<sup>a</sup> Laboratório de Química Orgânica, Departamento de Engenharia Química and Centro de Investigação de Engenharia Química e Biotecnologia, Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, Lisboa, Portugal

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# Studies Towards the Living Polymerisation of Phenylethynyl-calix[4]arene Compounds with Rh-based Ternary Catalytic Systems

ALEXANDRA I. COSTA and JOSÉ V. PRATA\*

Laboratório de Química Orgânica, Departamento de Engenharia Química and Centro de Investigação de Engenharia Química e Biotecnologia, Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, R. Conselheiro Emídio Navarro, 1, 1950-062 Lisboa, Portugal

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Dedicated to Professor Sundaresan Prabhakar on the occasion of his 70th birthday

The living polymerisation of mono and difunctional phenylethynylcalix[4]arene compounds **1** and **2** by Rh(I) ternary catalytic systems (TCS) was examined. Two TCS were tentatively prepared *in situ*, adapting known methodologies: (1) Rh(C≡CPh)(norbornadiene)(PPh<sub>3</sub>) and (2) Rh(C(Ph)C≡CPh<sub>2</sub>)(norbornadiene)(PPh<sub>3</sub>). Using the first TCS, the conjugated polymers poly **1** and poly **2** could be obtained in very good yields (77–86%), in short reaction times and freed from low-molecular-weight products, only when NEt<sub>3</sub> was used as a co-catalyst. With the second TCS, excellent results were obtained. Indeed, this catalytic system proved to be quite efficient in the polymerisation of calix[4]arenes **1** and **2**, affording the correspondent poly **1** and poly **2** essentially in almost quantitative yields (by GPC analysis), under appropriate conditions. The living nature of the polymerisation has been proved. For instance, in the case of calix[4]arene **1**, the  $M_n$  of the polymer obtained at high monomer conversion increased proportionally with the [1]:[Rh] molar ratio in the feed, keeping [1]<sub>0</sub> constant, thus showing that irreversible chain transfer or termination reactions did not occur to a major extent. Under the most favourable conditions {[1]:[Rh] = 50 and [2]:[Rh] = 50}, the polydispersities of poly **1** and poly **2** were kept in a narrow range (1.16–1.30).

**Keywords:** Calixarene; Conjugated polymers; Living polymerisation; rhodium; Transition metal catalyst; Dimerisation

## INTRODUCTION

The ability of conjugated polymers, incorporating macrocyclic receptors within their structure, to behave as specific chemical and biological sensors

has been recognised [1–8]. The sensory chemistry developed within these systems relies on the host–guest interactions transduced into a measurable response, which could be assessed by several analytical methods. It has been shown that the higher sensitivity of conjugated polymer-based sensors, when compared with those built up from single receptor molecules, is based on cooperative effects developed between the polymer framework and the molecular or ionic recognition sites of the macrocyclic receptors, which generate a higher signal amplification [9,10]. Several types of receptors (e.g. crown and azacrown ethers [11], cyclodextrins [12,13], calixarenes [7,14]) have been used for this purpose. In spite of the large body of knowledge that has been accumulated in regard to the ionic, molecular and biomolecular recognition abilities of single calixarene compounds [15], only a few studies have so far tackled the potential use of these cyclic oligomeric units as components of larger polymeric assemblies in which the photo/electroluminescence or magnetic properties of a conjugated main chain could provide the necessary transduction element to the sensory device. To the best of our knowledge, only three examples have been reported in which a calixarene unit is part of the polymeric conjugated chain. In one case, an upper rim monosubstituted derivative of calix[4]arene, possessing a diiodo functionality, was copolymerised with a 1,4-diethynylphenyl compound,

\*Corresponding author. E-mail: jvprata@deq.isel.ipl.pt

producing a poly(phenylene ethynylene)-type copolymer ( $M_n = 14,000$ , polydispersity index (PDI) = 1.8) [7]. Two other reports, also by the group of Swager, focus on the use of polythiophene [14] and poly(phenylene bithiophene)-type [16] polymers. Both syntheses involved the tethering of bithiophene moieties through a short spacer to the calixarene scaffold at the lower rim followed by a Stille-type [14] or Suzuki-type [16] cross-coupling polymerisation with appropriate difunctional compounds. In the former case, the  $M_n$  of the polymers (two examples) range from 22,000 to 47,000  $\text{g mol}^{-1}$  (PDI = 1.6–1.7), while in the other an oligomeric material was obtained ( $M_n = 4500$ , PDI = 1.55). In these works, it has been shown that a selective interaction occurs with some metal ions and the reduced/enhanced fluorescence of the conjugated polymer correlated with the host–guest interactions developed.

The same group as very recently [17] reported on the synthesis of poly(alkyl ethynyl) derivatives of calix[4]arenes using a Pd(II)/CuI-mediated homocoupling. However, they found that only the fixed partial cone conformations of the calixarene monomers were able to polymerise. None of the correspondent structures in the cone conformation yield any polymer. Instead, oligomers were formed. Besides, polymerisation did not work at all with unprotected calix[4]arenes (free phenolic groups present).

Our approach to this type of potential sensory systems is based in one hand on calix[4]arene compounds, working as the molecular or ionic recognition sites and, on the other, the photo- or electroluminescent properties of a conjugated poly(phenylacetylene)-type polymer. Since the proximity effects of the recognition site and the element responsible for the transduction of the signal to any measurable device are regarded by us as of utmost importance, the design of our calixarene monomers have taken this feature into account. That is to say that, contrary to a route that could involve the grafting of a specific calixarene unit to a functionalisable preformed conjugated polymer, we have favoured the way in which the polymer is synthesised directly from the calixarene-containing monomeric units. Our synthetic approach to this type of systems, involving the difunctional calix[4]arene derivative **1**, has been disclosed in a previous report [18]. Under a variety of conditions, conjugated polymers having a calixarene receptor incorporated into the main chain were obtained. When we tried to extend the above polymerisation method to a monosubstituted calix[4]arene analogue (**2**), huge amounts of oligomeric materials were retrieved or low polymerisation conversions were obtained. Even in the case of calix[4]arene **1**, the polymerisation is slow and, above all, neither the molecular weight of the polymer nor its

molecular weight distribution (MWD) was, in any event, controlled. Thus, it seemed to us that better polymerisation methodologies should be developed for this type of macrocyclic compounds in order to overcome the limitations expressed above and therefore potentiate their use as unique materials for a large field of applications such as electrochemical switches, electronic and optoelectronic devices and sensors. The synthetic work towards these main goals is described below.

## EXPERIMENTAL

### Materials and Methods

Melting points were measured in sealed capillaries using a Büchi 530 apparatus and are reported uncorrected. The melting temperatures of the monomers were determined by differential scanning calorimetry (DSC) using a Netzsch Luxx STA 409 PC, with a heating rate of  $7^\circ\text{C}/\text{min}$  under nitrogen. Infrared spectra (FT-IR) were recorded on a Bruker Vertex 70 using KBr pellets (transmission mode) at a resolution of  $2\text{ cm}^{-1}$ .  $^1\text{H}$  NMR and H-decoupled  $^{13}\text{C}$  NMR were recorded on a Bruker ARX 400 spectrometer ( $^1\text{H}$ , 400 MHz;  $^{13}\text{C}$ , 100 MHz) and the reported chemical shifts ( $\delta(\text{ppm})$ ) are internally referenced to tetramethylsilane ( $^1\text{H}$ ) and  $\text{CD}_2\text{Cl}_2/\text{CDCl}_3$  ( $^{13}\text{C}$ , 53.8 and 77.0 ppm relative to  $\text{Me}_4\text{Si}$ ). Elemental analyses were performed at the Microanalyses Services of Universidad de Vigo (C. A. C. T. I.) and Laboratório de Análises of Instituto Superior Técnico. High-resolution mass spectra were obtained at Instituto Tecnológico e Nuclear on a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (Finnigan FT/MS 2001-DT, equipped with a 3-Tesla superconducting magnet; electron ionisation (EI, 10 eV) at  $\sim 300^\circ\text{C}$ ) and at Faculdade de Ciências da Universidade de Lisboa on a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (Bruker Daltonics, APEX Qe FT-ICR, equipped with a 7-Tesla superconducting magnet; ESI mode). UV–Vis spectra were recorded on a Nicolet Evolution 300 spectrometer at  $5.0 \times 10^{-5}\text{ M}$  in  $\text{CHCl}_3$ . Gel permeation chromatography (GPC) was performed on a Jasco liquid chromatograph system equipped with a Jasco refractive index detector 2031 plus and a Jasco UV absorption detector 1575 (selected to 270 nm), using Polymer Standards Service SDV columns ( $10^3$  and  $10^5\text{ \AA}$ ) and THF as eluent at  $35^\circ\text{C}$ . Calibration was done with monodisperse polystyrene standards. The polymeric, oligomeric and dimeric contents of the polymerisation mixtures, the degrees of conversion and the final composition of the isolated materials, as well as the number average ( $M_n$ ) and weight average ( $M_w$ ) molecular weights, were estimated from the

GPC traces, based on UV detection. The polymerisation yields were determined gravimetrically.

Analytical thin layer chromatography (TLC) was performed on E. Merck Kieselgel 60, F-254 silica gel 0.2-mm-thick plates. Flash column chromatography was done on E. Merck Kieselgel 60 (230–400  $\mu\text{m}$ ) silica gel. Pressure-rated reaction vials with PTFE-silicon caps were used for the Sonogashira couplings performed at 120°C.

Calix[4]arenes **1** [18] and **3** [19] were synthesised according to the reported methods and characterised by FT-IR,  $^1\text{H}$  NMR and microanalysis. 4-Iodobenzyl bromide (95%, Aldrich), (bicyclo[2.2.1]hepta-2,5-diene) chloro-rhodium(I) dimer ( $[\text{Rh}(\text{norborene})\text{Cl}]_2$ , Aldrich), 4-dimethylaminopyridine (4-DMAP, 99%, Aldrich), copper(I) iodide (98%, Aldrich), copper(I) chloride (97%, Fluka), dichlorobis(triphenylphosphine)palladium (II) (98%, Aldrich), tetrabutylammonium fluoride hydrate (98%, Aldrich), ethynyltrimethylsilane (98%, Fluka), palladium(II) acetate (47% as Pd, Fluka), *n*-butyllithium (*n*-BuLi, 1.6 and 2.5 M solution in hexanes, Aldrich), bromotriphenylethylene (98%, Acros) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA, 99%, Aldrich) were used as obtained. Triphenylphosphine (98%, Merck) was recrystallised from hexane, diethylamine (99%, Acros Organics) and triethylamine (99%, Riedel-de-Haën), were pre-dried with  $\text{CaH}_2$  and distilled under  $\text{N}_2$  and stored over molecular sieves until use. Also, phenylacetylene (98%, Aldrich) was pre-dried with  $\text{CaH}_2$  and distilled under  $\text{N}_2$  just before use. All other reagents and solvents were of reagent grade and were purified and dried by the standard methods. Organic extracts were dried over anhydrous magnesium sulphate.

### Synthesis of calix[4]arene monomers

#### *5,11,17,23-Tetrakis(1,1-dimethylethyl)-25-(4-iodobenzoyloxy)-26,27,28-tripropylcalix[4]arene (4)*

To a clear solution of tri-*O*-propyl-*p*-*tert*-butylcalix[4]arene **3** (2.00 g, 2.58 mmol) in dry THF (62 ml) at room temperature (RT), NaH (0.423 g, 10.6 mmol, 60% in mineral oil) was added in portions. The resulting suspension was refluxed with stirring under argon for 30 min and cooled to RT. 4-Iodobenzyl bromide (1.88 g, 6.01 mmol) was added and the white suspension was stirred at reflux under an inert atmosphere. After 24 h, the TLC control ( $\text{CHCl}_3$ :hexane, 1:1) revealed the completion of the reaction. The solvent was removed in a rotary evaporator and the residue partitioned with 5% aq. HCl (25 ml) and  $\text{CHCl}_3$  (3  $\times$  25 ml). The organic extracts were combined and the solvent removed. After vacuum drying, the residue obtained was chromatographed ( $\text{CHCl}_3$ :hexane, 1:2), yielding 2.06 g (80.5%) of a colourless solid which on

recrystallisation ( $\text{CH}_2\text{Cl}_2$ :MeOH) furnished colourless crystals; mp 149–151°C;  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 3042, 2963, 2872, 1602, 1590, 1484, 1205, 1008, 868, 802;  $\delta_{\text{H}}$  (ppm,  $\text{CDCl}_3$ ): 0.81 (6H, t,  $-\text{CH}_2-\text{CH}_3$ ,  $J = 7.4$  Hz), 0.96 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 0.99 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 1.02 (3H, t,  $-\text{CH}_2-\text{CH}_3$ ,  $J = 7.4$  Hz), 1.18 (18H, s,  $\text{C}(\text{CH}_3)_3$ ), 1.86 (4H, m,  $-\text{CH}_2-\text{CH}_3$ ), 1.98 (2H, m,  $-\text{CH}_2-\text{CH}_3$ ,  $J = 7.4$  Hz), 3.07 (2H, d,  $\text{ArCH}_2\text{Ar}$ ,  $J = 12.5$  Hz), 3.09 (2H, d,  $\text{ArCH}_2\text{Ar}$ ,  $J = 12.5$  Hz), 3.75 (6H, m,  $-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ ), 4.34 (2H, d,  $\text{ArCH}_2\text{Ar}$ ,  $J = 13.1$  Hz), 4.37 (2H, d,  $\text{ArCH}_2\text{Ar}$ ,  $J = 13.1$  Hz), 4.77 (2H, s,  $\text{ArOCH}_2\text{Ar}$ ), 6.62 (2H, s,  $\text{ArH}$ ), 6.66 (2H, s,  $\text{ArH}$ ), 6.90 (4H, s,  $\text{ArH}$ ), 7.24 and 7.71 (2H each, d each,  $\text{I-ArH}$ ,  $J = 8.1$  Hz);  $\delta_{\text{C}}$  (ppm,  $\text{CD}_2\text{Cl}_2$ ): 10.2, 10.7 (two  $-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ , ratio 2:1), 23.55, 23.9 (two  $-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ , ratio 2:1), 31.4, 31.55, 31.75 ( $\text{C}(\text{CH}_3)_3$  and  $-\text{CH}_2$ ), 34.0, 34.1, 34.2 (three  $\text{C}(\text{CH}_3)_3$ , ratio 2:1:1), 77.1, 77.2, 77.5 (two  $-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3$  and  $-\text{O}-\text{CH}_2-\text{Ar}$ ), 93.8 ( $-\text{ArC}-\text{I}$ ), 125.2, 125.4, 125.5, 125.7, 132.1, 133.6, 134.3, 134.8, 135.1, 137.6, 138.4, 144.5, 144.8, 145.0, 153.0, 153.7, 154.5 ( $\text{ArC}$  and  $\text{ArC}-\text{H}$ ) [fewer carbon signals than expected in the region 31–32 ppm (three  $\text{C}(\text{CH}_3)_3$  and two bridged  $\text{CH}_2$ ) due to accidental isochrony]. HR-MS (FT-ICR-MS, EI)  $m/z$ : 990.5002 ( $\text{M}^+$ ,  $\text{C}_{60}\text{H}_{79}\text{IO}_4$  requires 990.5018). Anal. calcd. for  $\text{C}_{60}\text{H}_{79}\text{IO}_4$ : C, 72.71; H, 8.03. Found: C, 72.98; H, 8.43.

#### *5,11,17,23-Tetrakis(1,1-dimethylethyl)-25-(4-trimethylsilylethynyl)benzyloxy)-26,27,28-tripropylcalix[4]arene (5)*

**Procedure A.** To a stirred solution of **4** (200 mg, 0.202 mmol) in 0.8 ml of dry  $\text{NEt}_3$  under argon at RT was successively added  $\text{Pd}(\text{OAc})_2$  (1.2 mg, 5.1  $\mu\text{mol}$ ),  $\text{CuI}$  (1.92 mg, 10.1  $\mu\text{mol}$ ) and  $\text{PPh}_3$  (2.65 mg, 10.1  $\mu\text{mol}$ ). The clear pale yellow solution that results was kept at RT for 1 h with stirring. After that time,  $(\text{CH}_3)_3\text{SiC}\equiv\text{CH}$  (34  $\mu\text{l}$ , 0.242 mmol) was added to the slightly turbid greenish yellow solution that has been formed. The reaction mixture, which has acquired a dark brown colour, was then stirred at 50°C under an inert atmosphere. After 24 h, TLC control ( $\text{CH}_2\text{Cl}_2$ :hexane, 1:4; two elutions) indicated an essentially complete reaction. The contents of the flask were filtered and the solids washed with  $\text{CH}_2\text{Cl}_2$ . The filtrate was evaporated to dryness in a rotary evaporator. The dark brown residue was taken in  $\text{CH}_2\text{Cl}_2$  and washed twice with a saturated  $\text{NH}_4\text{Cl}$  solution. The organic extract was dried, the solvent removed and the residue dried under vacuum, yielding 166.5 mg of a crude product in almost pure state (TLC,  $^1\text{H}$  NMR). Flash chromatography ( $\text{CH}_2\text{Cl}_2$ :hexane, 1:3) furnished 80.2% of **5** as a colourless solid. Colourless crystals were obtained upon recrystallisation from  $\text{CH}_2\text{Cl}_2$ :MeOH; mp 198–199°C;  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 3033, 2963, 2875, 2158, 1603, 1581, 1480, 1249, 1205, 1123, 1010, 868, 842, 760;  $\delta_{\text{H}}$

(ppm, CDCl<sub>3</sub>): 0.27 (9H, s, Si(CH<sub>3</sub>)<sub>3</sub>), 0.84 (6H, t, -CH<sub>2</sub>-CH<sub>3</sub>, *J* = 7.5 Hz), 0.97 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 0.99 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.02 (3H, t, -CH<sub>2</sub>-CH<sub>3</sub>, *J* = 7.5 Hz), 1.18 (18H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.89 (4H, m, -CH<sub>2</sub>-CH<sub>3</sub>), 2.00 (2H, m, -CH<sub>2</sub>-CH<sub>3</sub>, *J* = 7.5 Hz), 3.04 (2H, d, ArCH<sub>2</sub>-Ar, *J* = 12.5 Hz), 3.10 (2H, d, ArCH<sub>2</sub>Ar, *J* = 12.5 Hz), 3.76 (6H, m, -O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 4.33 (2H, d, ArCH<sub>2</sub>Ar, *J* = 12.5 Hz), 4.38 (2H, d, ArCH<sub>2</sub>Ar, *J* = 12.5 Hz), 4.82 (2H, s, ArOCH<sub>2</sub>Ar), 6.63 (2H, s, ArH), 6.65 (2H, s, ArH), 6.89 (4H, s, ArH), 7.39 and 7.46 (2H each, d each, (CH<sub>3</sub>)<sub>3</sub>SiC≡C-ArH, *J* = 8.0 Hz); δ<sub>C</sub> (ppm, CD<sub>2</sub>Cl<sub>2</sub>): 0.03 (-Si(CH<sub>3</sub>)<sub>3</sub>), 10.2, 10.7 (two -O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, ratio 2:1), 23.6, 23.9 (two -O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, ratio 2:1), 31.4, 31.55, 31.7 (C(CH<sub>3</sub>)<sub>3</sub> and -CH<sub>2</sub>), 34.0, 34.1, 34.2 (three C(CH<sub>3</sub>)<sub>3</sub>, ratio 2:1:1), 77.2, 77.25 (shoulder), 77.5 (two -O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub> and -O-CH<sub>2</sub>-Ar), 94.5 (Ar-C≡C-Si(CH<sub>3</sub>)<sub>3</sub>), 105.4 (Ar-C≡C-Si(CH<sub>3</sub>)<sub>3</sub>), 123.0, 125.2, 125.3, 125.5, 125.6, 130.0, 131.9, 133.67, 133.695, 134.8, 135.0, 139.2, 144.5, 144.8, 145.0, 152.9, 153.7, 154.5 (ArC and ArC-H) [fewer carbon signals than expected in the region 31–32 ppm (three C(CH<sub>3</sub>)<sub>3</sub> and two bridged CH<sub>2</sub>) due to accidental isochrony]. HR-MS (FT-ICR-MS, EI) *m/z*: 960.6470 (M<sup>+</sup>, C<sub>65</sub>H<sub>88</sub>O<sub>4</sub>Si requires 960.6446). Anal. calcd. for C<sub>65</sub>H<sub>88</sub>O<sub>4</sub>Si·1.5H<sub>2</sub>O: C, 78.98; H, 9.28. Found: C, 78.68; H, 9.35. The presence of water was qualitatively confirmed by the <sup>1</sup>H NMR spectrum.

**Procedure B.** The previously reported procedure for the diethynylation of 1,3-bis-(4-iodobenzoyloxy)-calix[4]arene was followed [18]. Under those particular conditions, it proved to be inferior to the one described in this work.

#### 5,11,17,23-Tetrakis(1,1-dimethylethyl)-25-(4-ethynylbenzyloxy)-26,27,28-tripropoxy-calix[4]arene (2)

Calix[4]arene **5** (585.6 mg, 0.609 mmol) was first solubilised in THF (3 ml) and then dry MeOH (11 ml) and anhydrous potassium carbonate (8.42 mg, 0.061 mmol) were added. The mixture was stirred at 25°C under argon. The hydrolysis was followed by TLC (CH<sub>2</sub>Cl<sub>2</sub>:hexane, 1:1) and FT-IR. After 22 h, the reaction was worked up. The solvents were evaporated and the residual yellow mass was taken in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) and extracted with H<sub>2</sub>O (10 ml). The aqueous phase was back-extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 ml) and the combined organic extracts dried. After solvent removal and drying in vacuum, compound **2** was obtained in 86.3% as a yellowish white solid in pure state (TLC, GPC, <sup>1</sup>H NMR). Whenever necessary, this compound was chromatographed (CH<sub>2</sub>Cl<sub>2</sub>:hexane, 2:1); *t*<sub>m</sub> DSC 157.5 (onset 150.5°C); recrystallisation from CH<sub>2</sub>Cl<sub>2</sub>:MeOH furnished colourless crystals; mp 146–148°C; ν<sub>max</sub> (cm<sup>-1</sup>): 3309, 3270, 3033, 2963, 2871, 2112, 1603, 1583, 1481, 1202, 1123, 1008, 871, 823; λ<sub>max</sub>

(nm, ε<sub>max</sub> × 10<sup>-3</sup> M<sup>-1</sup> cm<sup>-1</sup>): 276 (4.3), 282 (4.3); δ<sub>H</sub> (ppm, CDCl<sub>3</sub>): 0.81 (6H, t, -CH<sub>2</sub>-CH<sub>3</sub>, *J* = 7.4 Hz), 0.95 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 0.98 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.02 (3H, t, -CH<sub>2</sub>-CH<sub>3</sub>, *J* = 7.4 Hz), 1.18 (18H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.87 (4H, m, -CH<sub>2</sub>-CH<sub>3</sub>), 1.98 (2H, m, -CH<sub>2</sub>-CH<sub>3</sub>, *J* = 7.5 Hz), 3.07 (2H, d, ArCH<sub>2</sub>Ar, *J* = 12.1 Hz), 3.09 (1H, s, ≡CH), 3.09 (2H, d, ArCH<sub>2</sub>Ar, *J* = 12.1 Hz), 3.75 (6H, m, -O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 4.35 (2H, d, ArCH<sub>2</sub>Ar, *J* = 12.1 Hz), 4.38 (2H, d, ArCH<sub>2</sub>Ar, *J* = 12.1 Hz), 4.82 (2H, s, ArOCH<sub>2</sub>Ar), 6.61 (2H, s, ArH), 6.65 (2H, s, ArH), 6.91 (4H, s, ArH), 7.45 and 7.50 (2H each, d each, HC≡C-ArH, *J* = 7.9 Hz); δ<sub>C</sub> (ppm, CD<sub>2</sub>Cl<sub>2</sub>): 10.2, 10.7 (two -O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, ratio 2:1), 23.5, 23.9 (two -O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, ratio 2:1), 31.4, 31.5, 31.75 (C(CH<sub>3</sub>)<sub>3</sub> and -CH<sub>2</sub>), 34.0, 34.1, 34.2 (three C(CH<sub>3</sub>)<sub>3</sub>, ratio 2:1:1), 77.2, 77.3, 77.45, 77.5 (two -O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, -O-CH<sub>2</sub>-Ar and Ar-C≡C-H), 83.9 (Ar-C≡C-H), 121.9, 125.2, 125.4, 125.5, 125.7, 130.1, 132.2, 133.60 (shoulder), 133.62, 134.8, 135.1, 139.6, 144.5, 144.8, 145.0, 152.95, 153.7, 154.5 (ArC and ArC-H) [fewer carbon signals than expected in the region 30–31.5 ppm (three C(CH<sub>3</sub>)<sub>3</sub> and two bridged CH<sub>2</sub>) due to accidental isochrony; running the <sup>13</sup>C spectrum in CDCl<sub>3</sub>, the signals corresponding to -CH<sub>2</sub>- appeared at 31.1 and 31.2 ppm]. HR-MS (FT-ICR-MS, EI) *m/z*: 888.6094 (M<sup>+</sup>, C<sub>62</sub>H<sub>80</sub>O<sub>4</sub> requires 888.6051). Anal. calcd. for C<sub>62</sub>H<sub>80</sub>O<sub>4</sub>·0.5H<sub>2</sub>O: C, 82.90; H, 9.09. Found: C, 83.19; H, 9.55. The presence of water was qualitatively confirmed in the <sup>1</sup>H NMR spectrum.

The removal of the Si(CH<sub>3</sub>)<sub>3</sub> group was also accomplished with *n*-Bu<sub>4</sub>NF/THF, at 25°C for 30 min–1 h, in the same manner as described before for bis-trimethylsilylethynyl derivative of calix[4]-arene **1** [18].

#### Biscalix[4]arene 6

To a colourless solution of compound **2** (50 mg, 56 μmol) in dry toluene (560 μl) at RT was added copper(I) chloride (0.29 mg, 2.8 μmol), under stirring. The solution turned yellow and then gradually to greenish blue with turbidity. Immediately following, TMEDA (0.5 μl, 3.2 μmol) was added and the suspension introduced in a pre-heated bath at 60°C for 1.5 h. The contents were evaporated in a rotary evaporator and the residue taken in CH<sub>2</sub>Cl<sub>2</sub> and washed with 10% aq. HCl and water. The organic extract was dried, the solvent removed and the residue dried in vacuum, giving a crude product in 70% [chromatographically pure, TLC (CHCl<sub>3</sub>:hexane, 1:1)]. In order to remove possible copper compounds, the solid was redissolved in CH<sub>2</sub>Cl<sub>2</sub> and washed successively with 0.1 M NaHSO<sub>3</sub>, 10% aq. NH<sub>4</sub>SCN and water. After drying the organic extract, solvent evaporation and drying in vacuum, compound **6** was obtained in 45.2% as an almost colourless solid; trituration with MeOH furnished a colourless solid; mp 174–176°C; ν<sub>max</sub> (cm<sup>-1</sup>): 3036, 2960, 2875, 1604,

TABLE I Rh (I)-catalysed polymerisation of calix[4]arene **2** with binary catalytic systems<sup>a,b</sup>.

Entry	Solvent	[ <b>2</b> ]	[ <b>2</b> ]:[Rh]	Co-catalyst (eq./[Rh])	Time (h)	Conversion (%) <sup>b</sup>	Reaction mixture composition (%) <sup>b</sup>			$M_n \times 10^{-4}$ ( $M_w/M_n$ ) <sup>c</sup>
							Polymer	Oligomers	Dimer	
1	THF	0.2	25	PPh <sub>3</sub> (2)	4.5 <sup>d</sup>	40.7	31.5	3.8	5.4	7.1 (2.31)
2	THF	0.05	50	NHEt <sub>2</sub> (100)	18.5 <sup>d</sup>	48.3	1.6	41.9	4.8	6.0 (1.32)
3	THF	0.05	50	NEt <sub>3</sub> (100)	20 <sup>d</sup>	66.7	2.9	57.7	6.2	– <sup>e</sup>
4	CHCl <sub>3</sub>	0.07	25	NHEt <sub>2</sub> (25)	23	90.9	60.9	27.8	2.2	– <sup>e</sup>
5	CHCl <sub>3</sub>	0.1	50	NHEt <sub>2</sub> (50)	6 <sup>d</sup>	40.8	14.8	22.4	3.6	– <sup>e</sup>
6	CHCl <sub>3</sub>	0.05	50	NHEt <sub>2</sub> (50)	24	94.1	19.2	69.6	5.7	– <sup>e</sup>
7	THF	0.1	50	<i>n</i> -BuLi (2.5) <sup>f</sup>	1	19.4	14.1	2.5	2.8	4.6 (2.51)

<sup>a</sup> Typical conditions: Monomer **2**, [Rh(nbd)Cl]<sub>2</sub>, solvent and co-catalyst, 30°C; <sup>b</sup> The degree of conversion and the composition of the polymerisation mixture were evaluated by GPC; <sup>c</sup> The  $M_n$  and polydispersity ( $M_w/M_n$ ) were determined by GPC (THF, 35°C, polystyrene standards) and are referred to polymeric materials; <sup>d</sup> The reaction was quenched at this time due to its high viscosity, which had preventing adequate stirring of its contents; <sup>e</sup> Bimodal/multimodal distribution; <sup>f</sup> PPh<sub>3</sub> was also added ([phosphine]:[Rh] = 5).

1583, 1482, 1202, 1122, 1009, 870, 820;  $\lambda_{\max}$  (nm,  $\epsilon_{\max} \times 10^{-5} \text{ M}^{-1} \text{ cm}^{-1}$ ): 298 (3.6), 316 (4.9), 338 (4.3);  $\delta_{\text{H}}$  (ppm, CDCl<sub>3</sub>): 0.82 (12H, t,  $-\text{CH}_2-\text{CH}_3$ ,  $J = 7.5 \text{ Hz}$ ), 0.96 (18H, s,  $\text{C}(\text{CH}_3)_3$ ), 0.995 (18H, s,  $\text{C}(\text{CH}_3)_3$ ), 1.02 (6H, t,  $-\text{CH}_2-\text{CH}_3$ ,  $J = 7.5 \text{ Hz}$ ), 1.18 (36H, s,  $\text{C}(\text{CH}_3)_3$ ), 1.88 (8H, m,  $-\text{CH}_2-\text{CH}_3$ ), 1.98 (4H, m,  $-\text{CH}_2-\text{CH}_3$ ,  $J = 7.5 \text{ Hz}$ ), 3.08 (4H, d,  $\text{ArCH}_2\text{Ar}$ ,  $J = 12.4 \text{ Hz}$ ), 3.10 (4H, d,  $\text{ArCH}_2\text{Ar}$ ,  $J = 12.4 \text{ Hz}$ ), 3.75 (12H, m,  $-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ ), 4.36 (4H, d,  $\text{ArCH}_2\text{Ar}$ ,  $J = 12.1 \text{ Hz}$ ), 4.38 (4H, d,  $\text{ArCH}_2\text{Ar}$ ,  $J = 12.1 \text{ Hz}$ ), 4.83 (4H, s,  $\text{ArOCH}_2\text{Ar}$ ), 6.62 (4H, s,  $\text{ArH}$ ), 6.66 (4H, s,  $\text{ArH}$ ), 6.90 (8H, s,  $\text{ArH}$ ), 7.47 and 7.55 (4H each, d each,  $\text{ArH}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{ArH}$ ,  $J = 8.0 \text{ Hz}$ );  $\delta_{\text{C}}$  (ppm, CD<sub>2</sub>Cl<sub>2</sub>): 10.2, 10.7 (two  $-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ , ratio 2:1), 23.6, 23.9 (two  $-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ , ratio 2:1), 31.4, 31.5, 31.7 ( $\text{C}(\text{CH}_3)_3$  and  $-\text{CH}_2$ ), 34.0, 34.1, 34.2 (three  $\text{C}(\text{CH}_3)_3$ , ratio 2:1:1), 74.15, 77.2, 77.5 ( $-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ ,  $-\text{O}-\text{CH}_2-\text{Ar}$  and  $\text{Ar}-\text{C}\equiv\text{C}-\text{C}\equiv\text{CAr}$ ), 82.0 ( $\text{Ar}-\text{C}\equiv\text{C}-\text{C}\equiv\text{CAr}$ ), 121.4, 125.2, 125.4, 125.5, 125.7, 130.2, 132.6, 133.65, 134.8, 135.05, 140.2, 144.5, 144.8, 145.1, 153.0, 153.7, 154.5 ( $\text{ArC}$  and  $\text{ArC}-\text{H}$ ) [fewer carbon signals than expected in the region 31–32 ppm (three  $\text{C}(\text{CH}_3)_3$  and two bridged  $\text{CH}_2$ ), 70–80 ppm (two  $-\text{OCH}_2\text{CH}_2\text{CH}_3$ ,  $-\text{OCH}_2-\text{Ar}$  and  $\text{Ar}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{Ar}$ ) and 133–134 ppm (two  $\text{ArC}$ ) due to accidental isochrony; running the <sup>13</sup>C spectrum in CDCl<sub>3</sub>, the signals pertaining to  $-\text{CH}_2-$  appeared at 31.4 and 31.5 ppm and those of  $\text{ArC}$  at 133.40 and 133.45 ppm]. HR-MS (ESI-FT-ICR-MS)  $m/z$ : 1798.18335 ( $[\text{M}-\text{Na}]^+$ ,  $\text{C}_{124}\text{H}_{158}\text{O}_8\text{Na}$  requires 1798.1849). Anal. calcd. for  $\text{C}_{124}\text{H}_{158}\text{O}_8 \cdot \text{H}_2\text{O}$ : C, 82.99; H, 8.99. Found: C, 82.87; H, 9.57. The presence of water was qualitatively confirmed by the <sup>1</sup>H NMR spectrum.

#### General Procedure for the Polymerisation of Calix[4]arene **2** using Binary Catalyst Systems

All the polymerisations were carried out in septum-sealed dry glass vials under an argon atmosphere. To a solution containing 0.104 mg (0.225  $\mu\text{mol}$ ) of [Rh(nbd)Cl]<sub>2</sub> in dry THF (16  $\mu\text{l}$ ) was added 0.236 mg

(0.9  $\mu\text{mol}$ ) of PPh<sub>3</sub>. The yellow solution was deaerated with argon and the tube sealed. After a stirring period of 0.5 h at 30°C, an argon-deaerated solution of 10.0 mg (11.2  $\mu\text{mol}$ ) of monomer **2** in dry THF (40  $\mu\text{l}$ ) was added through syringe under argon. The mixture was then stirred at 30°C for a certain time, progressively acquiring an intense orange/reddish colour. The polymerisation mixture was quenched with a large excess of acetic acid (*ca.* 200 mol eq. of Rh) and stirred for 20–30 min. The GPC analysis was performed on samples withdrawn from the crude mixture at appropriate times. The remaining contents were precipitated by the addition of methanol. The orange precipitate was filtered and dried in a vacuum oven at 65°C. The above procedure refers to the preparation of **poly 2** under the conditions of entry 1, Table I (see results and discussion section). Other conditions employed for the polymerisation of **2** are also found in the table.

#### General Procedure for the Polymerisation of Calix[4]arene **1** and **2** using Ternary Catalyst Systems prepared *in situ*

##### Ternary Catalytic System I (TCS I)

The reference TCS I used in this work was prepared *in situ* according to a modified literature procedure [20,21].

1. Preparation of the Rh initiator *in situ*. A solution of phenylacetylene (35  $\mu\text{l}$ , 0.313 mmol) in dry toluene (350  $\mu\text{l}$ ) was placed in a septum-sealed tube under argon and cooled in an ice bath. A cooled *n*-BuLi solution (2.5 M in hexane; 126  $\mu\text{l}$ , 0.313 mmol, in 350  $\mu\text{l}$  of dry toluene) was then added dropwise through a syringe and the light yellow solution stirred at 0°C for 15 min. [Rh(nbd)Cl]<sub>2</sub> (78  $\mu\text{g}$ , 0.17  $\mu\text{mol}$ ), triphenylphosphine (0.44 mg, 1.7  $\mu\text{mol}$ ) and 4-DMAP (0.1 mg, 0.85  $\mu\text{mol}$ ) placed in another septum-sealed tube under argon and dry toluene (45  $\mu\text{l}$ ) was added through a syringe.

TABLE II Rh (I)-catalysed polymerisation of calix[4]arenes **1** and **2** with TCS I<sup>a,b</sup>.

Entry	Monomer	[PhC≡CLi]:[Rh]	Additive (eq./[Rh])	Time (h)	Conversion (%) <sup>b</sup>	Reaction mixture composition (%) <sup>b</sup>			$M_n \times 10^{-4}$ ( $M_w/M_n$ ) <sup>c,d</sup>
						Polymer	Oligomers	Dimer	
1	2	3.1 <sup>e</sup>	4-DMAP (2.5)	1	41.3	40.5	–	0.8	5.0 (1.53)
				3	56.0	55.3	–	0.7	5.7 (2.13)
2	2	3.1 <sup>e,f</sup>	4-DMAP (2.5)	1	23.5	22.1	–	1.4	3.9 (1.34)
				4	54.2	50.5	0.6	0.8	5.3 (1.79)
3	2	9.4 <sup>e,f</sup>	4-DMAP (2.5)	1	28.7	27.9	0.1	0.7	3.8 (1.41)
				4	49.3	46.8	0.8	1.7	5.2 (1.82)
4	2	15.6 <sup>e,f</sup>	4-DMAP (2.5)	1	36.6	35.4	0.3	0.9	4.0 (1.40)
				4	54.7	53.0	0.4	1.3	4.8 (1.87)
5	2	3.1 <sup>e,g</sup>	4-DMAP (2.5)	1	51.6	50.7	–	0.9	2.7 (1.58)
				3	52.1	50.9	–	1.2	3.0 (1.72)
6	2	3.1 <sup>e,g</sup>	NEt <sub>3</sub> (25)	1	54.6	53.7	0.1	0.8	5.9 (1.49)
				3	70.7	69.6	0.2	0.9	8.0 (1.97)
7	2	3.1 <sup>e</sup>	NEt <sub>3</sub> (25)	1	86.4	85.3	0.3	0.8	6.4 (1.69)
				3	87.7	86.3	0.3	1.1	6.5 (1.89)
8	2	5	NEt <sub>3</sub> (25)	1	47.3	46.7	–	0.6	6.1 (1.53)
				3	69.1	68.1	–	1.0	7.8 (2.06)
9	2	10	NEt <sub>3</sub> (25)	1	46.6	46.1	–	0.5	4.7 (1.57)
				3	67.7	67.2	–	0.5	6.4 (2.06)
10	2	5	4-DMAP (2.5)	1	17.0	16.6	–	0.4	3.4 (1.41)
				3	33.2	32.8	–	0.4	4.5 (1.66)
11	2	5	NEt <sub>3</sub> (75)	1	66.4	65.6	–	0.8	5.7 (1.59)
				3	76.7	75.8	–	0.9	6.7 (2.00)
12	2	– <sup>h</sup>	NEt <sub>3</sub> (75)	1	3.2	2.9	–	0.3	3.5 (1.28)
				3	37.0	28.5	4.0	4.5	6.0 (1.43)
13	1	3.1 <sup>e</sup>	NEt <sub>3</sub> (25)	1	76.8	75.0	–	1.8	8.6 (1.82)

<sup>a</sup> Typical conditions: [2] = 0.1 M, [Rh(nbd)Cl]<sub>2</sub>/PhC≡CLi/PPh<sub>3</sub>, [2]:[Rh] = 50, [PPh<sub>3</sub>]:[Rh] = 5, toluene, 30°C; <sup>b</sup> The degree of conversion and the composition of the polymerisation mixture were evaluated by GPC; <sup>c</sup> Data refers to polymeric materials; <sup>d</sup> The  $M_n$  and polydispersity ( $M_w/M_n$ ) were determined by GPC (THF, 35°C, polystyrene standards); <sup>e</sup> Phenylacetylene was also present in the proportion: [PhC≡CH]:[PhC≡CLi] = 0.6; <sup>f</sup> No ageing period; <sup>g</sup> The catalytic system was aged at 30°C for 2 h; <sup>h</sup> A molar ratio of [PhC≡CH]:[Rh] = 5 was used.

The yellow solution was stirred for 15 min at RT and then cooled to –15°C. The toluene solution of phenylethynyllithium (4 μl) was added through a syringe. The catalyst mixture was stirred at –15°C for 15 min and then allowed to rise to 0°C and stirred for 2 h at this temperature, resulting in a pale yellow solution.

The above procedure refers to the conditions of entry 10, Table II. Other diverse conditions are reported in Table II.

2. Polymerisation procedure of calix[4]arenes **1** or **2** with TCS I. A solution of monomer **2** (15 mg, 16.9 μmol) in dry toluene (120 μl), contained in a septum-sealed tube under argon, was added dropwise through a syringe to the initiator solution. Stirring was continued for a certain time (Table II) at 30°C. During that period, the reaction mixture progressively acquired an orange/deep orange/reddish colour, depending on the extension of the polymerisation. Samples of the crude mixture were withdrawn after certain periods for GPC analysis, being previously quenched with an excess of acetic acid.

An identical procedure was followed for the polymerisation of calix[4]arene **1**.

### Ternary Catalytic System II (TCS II)

The reference TCS II used in this work was prepared according to a modified literature procedure [22, 23].

1. Preparation of the Rh initiator *in situ*. A solution of bromotriphenylethylene (67 mg, 0.2 mmol) in dry toluene (1 ml) contained in a septum-sealed tube under argon was cooled in an ice bath. A cooled *n*-BuLi solution (1.6 M in hexane; 127 μl, 0.2 mmol) was then added dropwise through a syringe. The resulting clear mixture acquired an intense yellow colour. A 0.1 M solution of triphenylvinylolithium was made by the addition of 0.87 ml of dry toluene, which was kept in an ice bath until use. [Rh(nbd)Cl]<sub>2</sub> (105 μg, 0.23 μmol) and triphenylphosphine (0.6 mg, 2.3 μmol) were placed in another septum-sealed tube under argon and dry toluene (71 μl) was added through a syringe. The triphenylvinylolithium solution (57 μl) was then added dropwise through a syringe to the catalyst solution, which immediately develops an intense yellow colour and the resulting mixture placed in a pre-heated bath at 30°C for 30 min.
2. Polymerisation procedure of calix[4]arenes **1** or **2** with TCS II. The monomer **1** (20 mg, 22.8 μmol) was

TABLE III Rh (I)-catalysed polymerisation of calix[4]arene **1** with TCS II<sup>a,b</sup>.

Entry	[1]:[Rh]	Time (h)	Conversion (%) <sup>b</sup>	Reaction mixture composition (%) <sup>a</sup>			Isolated materials <sup>b</sup>		
				Polymer	Oligomers	Dimer	Yield (%) <sup>c</sup>	Poly <b>1</b> (%) <sup>a</sup>	$M_n \times 10^{-4}$ ( $M_w/M_n$ ) <sup>d</sup>
1	25	9	99.2	98.8	–	0.4	64.5	98.7	1.8 (1.45)
2	50	9	99.1	98.0	0.4	0.7	53.5	98.4	2.8 (1.35)
3	100	9	94.4	90.9	1.8	1.7	56.0	94.6	5.2 (1.56)
4	150	9	79.4	74.2	2.9	2.3	52.0	77.9	6.0 (1.65)
5	50	1	97.1	96.3	–	0.8	76.5	98.4	2.3 (1.30)

<sup>a</sup>Typical conditions: [1] = 0.1 M, [Rh(nbd)Cl]<sub>2</sub>/Ph<sub>2</sub>C=CPhLi/PPh<sub>3</sub>, [PPh<sub>3</sub>]:[Rh] = 5, toluene, 30°C; <sup>b</sup>The degree of conversion, the composition of the polymerisation mixture and that of the isolated materials were evaluated by GPC. <sup>c</sup>Gravimetrically determined yield. <sup>d</sup>The  $M_n$  and polydispersity ( $M_w/M_n$ ) were determined by GPC (THF, 35°C, polystyrene standards). The data correspond to the polymer fraction of the isolated materials.

placed in a septum-sealed tube under argon and a solution made by the addition of dry toluene (100  $\mu$ l) at RT. This solution was added dropwise through a syringe to the initiator solution, acquiring almost instantaneously an intense orange colour. The polymerisation mixture was then kept at 30°C with vigorous stirring for a certain time (Tables III and IV). During that time, a colour deepening as well as a gradual increase in the viscosity of the reaction was observed. After the appropriate time, the polymerisation mixture was quenched with a large excess of acetic acid (200 mol eq. of Rh), stirred for 20–30 min and an aliquot withdrawn for the GPC analysis of the crude mixture. The polymer was isolated by the addition of methanol. The yellow precipitate was filtered, washed with methanol and dried in a vacuum oven at 65°C. The composition of the solids thus obtained was subsequently evaluated by the GPC.

The above procedure refers to the preparation of **poly 1** under the conditions of entries 1–5 of Table III. Identical procedure was used for the polymerisation of calix[4]arene **2** (Table IV). In this case, the polymerisation solution acquired a reddish/brown colour during the stirring period and an orange precipitate was obtained after the addition of methanol.

**Poly 1.** Obtained in 76.5% as a yellow solid;  $\nu_{\max}$  ( $\text{cm}^{-1}$ ): 3509, 3394, 3050, 3029, 2961, 2872, 1601, 1486, 1206, 1125, 1002, 875, 819;  $\lambda_{\max}$  (nm,  $\epsilon_{\max} \times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$ ): 280 (400), 400 (13) cut-off 525;  $\delta_{\text{H}}$  (ppm): 0.94 (br s, C(CH<sub>3</sub>)<sub>3</sub>), 1.26 (br s, C(CH<sub>3</sub>)<sub>3</sub>), 2.8–3.6 (br m, ArCH<sub>2</sub>Ar), 3.8–5.3 (br m, ArCH<sub>2</sub>Ar, ArOCH<sub>2</sub>Ar), 5.9 (br s, –CH=C–), 6.4–7.2 (br m, ArH), 7.2–7.6 (br m, –CH=C–ArH). Anal. calcd. for (C<sub>62</sub>H<sub>68</sub>O<sub>4</sub>)<sub>n</sub>: C, 84.89; H, 7.81. Found: C, 84.12; H, 7.99.

**Poly 2.** Obtained in 78.5% as an orange solid;  $\nu_{\max}$  ( $\text{cm}^{-1}$ ): 3046, 3025, 2961, 2871, 1605, 1584, 1482, 1202, 1125, 1011, 870, 815;  $\lambda_{\max}$  (nm,  $\epsilon_{\max} \times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$ ): 276 (210), 466 (8.3) cut-off 580;  $\delta_{\text{H}}$  (ppm): 0.8 (br m, –CH<sub>2</sub>–CH<sub>3</sub>, C(CH<sub>3</sub>)<sub>3</sub>), 1.25 (br s, C(CH<sub>3</sub>)<sub>3</sub>), 1.8 (br m, –CH<sub>2</sub>–CH<sub>3</sub>), 3.1 (br m, ArCH<sub>2</sub>Ar), 3.4–3.9 (br m, –O–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>3</sub>), 4.0–4.9 (br m, ArCH<sub>2</sub>Ar, ArOCH<sub>2</sub>Ar), 5.9 (br s, –CH=C–), 6.5 (br m, ArH), 7.0 (br m ArH), 7.2–7.6 (br m, –CH=C–ArH). Anal. calcd. for (C<sub>62</sub>H<sub>80</sub>O<sub>4</sub>)<sub>n</sub>: C, 83.74; H, 9.07. Found: C, 82.00; H, 9.33.

## RESULTS AND DISCUSSION

### Monomer Synthesis

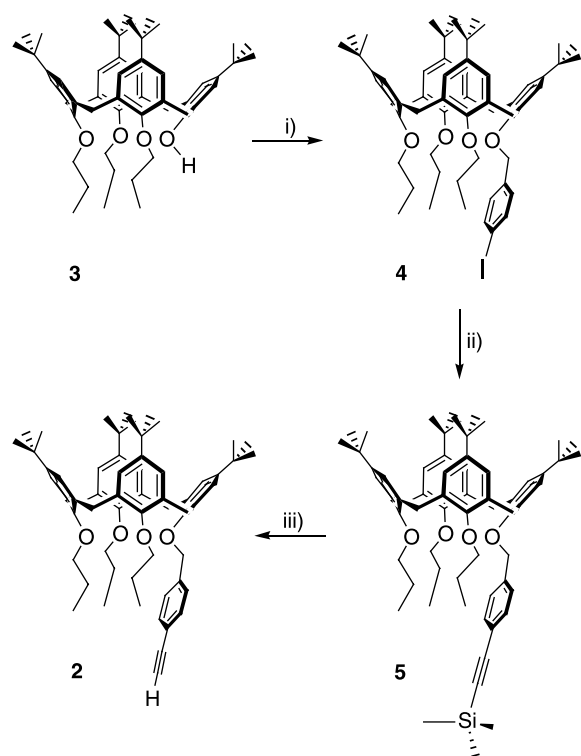
The synthetic route towards *syn*-1,3-bis(4-ethynylbenzyloxy)calix[4]arene **1** has been described before [18]. The tripropylated calixarene **2** was prepared in a similar fashion (Scheme 1).

TABLE IV Rh (I)-catalysed polymerisation of calix[4]arene **2** with TCS II<sup>a,b</sup>.

Entry	[2]:[Rh]	Time (h)	Conversion (%) <sup>b</sup>	Reaction mixture composition (%) <sup>b</sup>			Isolated materials <sup>b</sup>		
				Polymer	Oligomers	Dimer	Yield (%) <sup>c</sup>	Poly <b>2</b> (%) <sup>b</sup>	$M_n \times 10^{-4}$ ( $M_w/M_n$ ) <sup>d</sup>
1	25	1	95.8	94.9	–	0.9	56.0	96.5	1.3 (1.16)
2	50	1	97.7	97.5	–	0.2	78.5	99.3	1.6 (1.16)
3	100	0.66	87.0	86.3	–	0.7	59.0	84.6 <sup>e</sup>	4.3 (1.67)
4	150	0.66	87.3	86.6	–	0.7	65.5	85.5 <sup>f</sup>	4.4 (1.52)
5	50 <sup>g</sup>	1	97.6	97.3	–	0.3	82.5	97.9	1.7 (1.19)

<sup>a</sup>Typical conditions: [2] = 0.1 M, [Rh(nbd)Cl]<sub>2</sub>/Ph<sub>2</sub>C=CPhLi/PPh<sub>3</sub>, [PPh<sub>3</sub>]:[Rh] = 5, toluene, 30°C. <sup>b</sup>The degree of conversion, the composition of the polymerisation mixture and that of the isolated materials were evaluated by GPC. <sup>c</sup>Gravimetrically determined yield. <sup>d</sup>The  $M_n$  and polydispersity ( $M_w/M_n$ ) were determined by GPC (THF, 35°C, polystyrene standards). The data correspond to the polymer fraction of the isolated materials. <sup>e</sup>Additionally, a polymer (5.8%) with  $M_n = 1.0 \times 10^5$  ( $M_w/M_n = 1.18$ ) was present. <sup>f</sup>A polymer (9.9%) with  $M_n = 8.9 \times 10^4$  ( $M_w/M_n = 1.18$ ) was also present. <sup>g</sup>[2] = 0.05 M.





SCHEME 1 Synthesis of 25-(4-ethynylbenzyloxy)-26,27,28-tripropoxycalix[4]arene **2**: (i) BrCH<sub>2</sub>PhI (2.3 eq.), NaH (4.1 eq.), THF, reflux, 24 h; (ii) Pd(OAc)<sub>2</sub> (2.5 mol%), CuI (5 mol%), (CH<sub>3</sub>)<sub>3</sub>SiC≡CH (1.2 eq.), PPh<sub>3</sub> (5 mol%), NEt<sub>3</sub>, 50°C, 24 h; (iii) K<sub>2</sub>CO<sub>3</sub> (0.1 eq.), THF/MeOH, 25°C, 22 h.

Derivatisation of the parent calix[4]arene **3** with 4-iodobenzyl bromide in THF, using NaH as the base, afforded the intermediate iodo compound **4** in good yield (80.5%). The four sets of doublets appearing in the <sup>1</sup>H NMR spectrum at 3.07, 3.09 and 4.34, 4.37 ppm, respectively, with a  $\Delta\delta$  between the *exo* and *endo* protons around 1.3 ppm, unambiguously pointed to a cone conformer. Thereafter, calix[4]arene **4** was coupled with trimethylsilylacetylene, using the Sonogashira–Hagihara cross-coupling reaction [24, 25], in which Pd(OAc)<sub>2</sub> was used as the Pd(0) source, CuI as a co-catalyst and NEt<sub>3</sub> as the base/solvent. The protected ethynyl compound **5** was obtained in very good yield (86%) by a simple isolation procedure. Alternatively, the same reaction could be performed in a closed vessel with PdCl<sub>2</sub>[PPh<sub>3</sub>]<sub>2</sub>/CuI/NHEt<sub>2</sub> in THF at 120°C in much shorter reaction times. FT-IR spectrum of **5** showed a sharp carbon triple bond stretching frequency at 2158 cm<sup>-1</sup> and the characteristic frequencies of the Si(CH<sub>3</sub>)<sub>3</sub> group at 1249, 868, 842 and 760 cm<sup>-1</sup>, in addition to those of the calixarene moiety. The trimethylsilylethynyl derivative **5**

exhibited three separate singlet resonances (9H:9H:18H) for the *p-tert*-butyl groups and also for those corresponding to the aryl protons (2H:2H:4H), evidencing the presence of a symmetrical structure, bisecting the ethynyl derivative and the propyl group in the cone conformation. The *endo* and *exo* bridged methylene protons were observed as two separate sets of signals of each type [3.04, 3.10 and 4.33, 4.38 ppm;  $\Delta\delta$  (H<sub>*exo*</sub>–H<sub>*endo*</sub>) ~ 1.3 ppm]; the remaining signals are all consistent with the proposed structure for **5**.

Deprotection of the ethynyl group was typically effected under basic conditions (anhydrous K<sub>2</sub>CO<sub>3</sub>/MeOH/THF, 24 h, 25°C), yielding the ethynyl compound **2** in 86%. The removal of the Si(CH<sub>3</sub>)<sub>3</sub> group could also be done by the use of (*n*-butyl)<sub>4</sub>NF in THF, resulting in faster reactions (0.5–1 h, 25°C) and also good isolated yields. The new formed triple bond derivative showed its C≡C stretching vibration at 2112 cm<sup>-1</sup>, with a much lower intensity when compared with **5** and that of the ≡C–H appeared splitted in the two bands peaking at 3309 and 3270 cm<sup>-1</sup>. The ethynylic proton of **2** appears at 3.09 ppm and the bridged methylene resonances showed the same pattern as before.

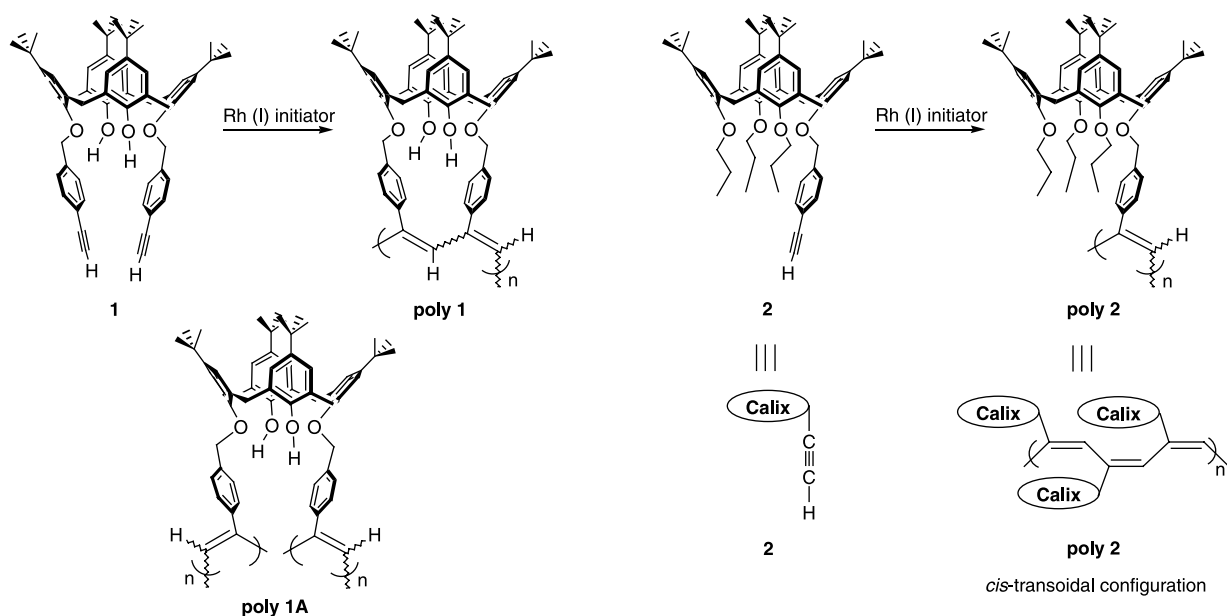
## Polymer synthesis

### Non-living Polymerisations

Rhodium(diene) complexes (either neutral or cationic) are known as outstanding catalysts for the polymerisation of monosubstituted acetylene derivatives, affording conjugated polymers [26, 27]. In addition, to the large range of solvents that can be used (from hydrocarbons, chlorinated hydrocarbons and ethers to alcohols, amines and even water) in these polymerisations, a wide range of monomers carrying a diversity of functional groups are highly compatible with this catalyst. In particular, Rh(I)-based catalysts efficiently polymerise phenylacetylene (PA) and many of its ring derivatives with remarkable stereoregularity and stereospecificity, leading typically to a head-to-tail *cis*-transoid chain arrangement, as a result of a *cis* insertion mechanism [28–31].

In a recent report [18], we have shown that difunctional calix[4]arene **1**, in its cone conformation, was preferentially polymerised with a binary catalytic system comprising [Rh(*nbd*)Cl]<sub>2</sub> and triphenylphosphine (as the sole additive) in THF at 30°C. High conversions and good isolated yields of the corresponding conjugated polymer **poly 1** (Scheme 2)<sup>1</sup> were obtained under these conditions

<sup>1</sup> Although the ring-closing polymerisation of **1**, through an alternating intra-intermolecular chain mechanism, would lead to the proposed structure for **poly 1**, [18] the alternative structure **poly 1A**, which would result from the independent linear polymerisation of each pendant acetylenic moiety, cannot be ruled out based on the available structural data. For the sake of simplicity, the polymer resultant from calix[4]arene **1** is referred as **poly 1** throughout the text.



SCHEME 2 Rh(I)-catalysed polymerisation of calix[4]arenes 1 and 2 and the possible structures of the resulting polymers<sup>1</sup>.

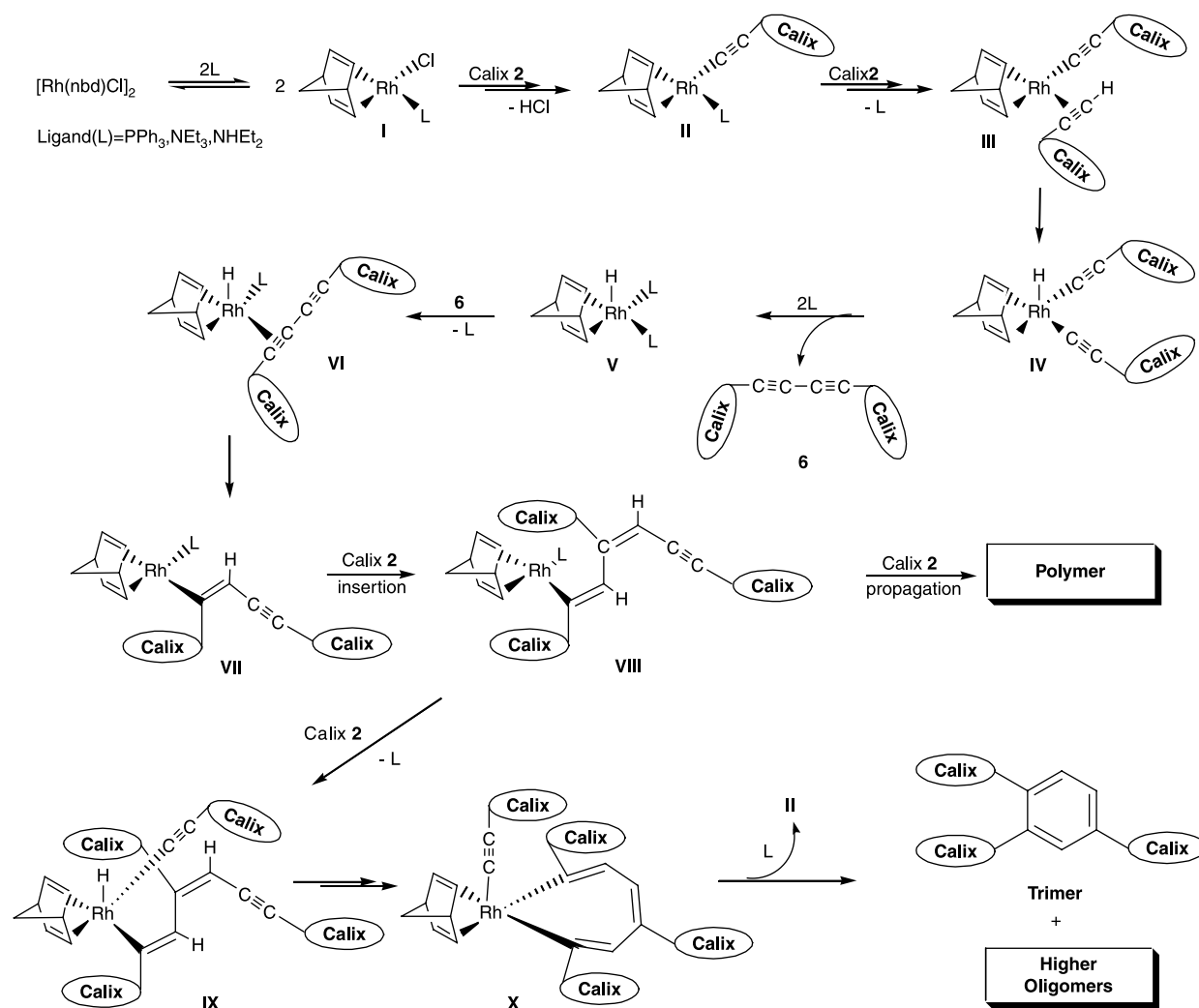
( $M_n = 8.8 \times 10^4$ ,  $M_w/M_n = 1.85$ ). It was found that increasing amounts of low-molecular-weight compounds (dimer and oligomers, up to almost 30%) were produced when other solvents ( $\text{CHCl}_3$  or toluene) or other co-catalysts ( $\text{NHEt}_2$ ) were used instead.

When the very same polymerisation conditions were applied to calixarene 2 (entry 1, Table I), the reaction stops stirring after 4.5 h resulting in low monomer conversion (*ca.* 40%) with significant amounts of dimer and oligomers being formed (*ca.* 10%), in addition to 31% of the polymer. The data shown in Table I illustrate some of the reaction parameters changed in order to overcome the aforementioned result. The use of amines ( $\text{NHEt}_2$  or  $\text{NEt}_3$ ) as co-catalysts proved much worse, whatever the solvent used. In these cases (entries 2–6), oligomeric materials were normally retrieved as the major products. When  $\text{NHEt}_2$  was used, the main oligomeric compound found in the polymerisation mixture seems, actually, to be a trimer [ $M_n = 2579$  ( $M_w/M_n = 1.02$ ), calculated  $M_n = 2668$ ]. It appears that its formation is more favoured when higher diluted solutions of the monomer are used (*cf.* entries 5 and 6). The nature of the amine does not appear to have any deep influence on the conversion or on the polymer yield (entries 2 and 3). The use of *n*-BuLi in conjunction with  $\text{PPh}_3$  did not bring any improvement to the overall polymerisation performance [32].

The expected polymer (**poly 2**) was normally obtained in very low yields, showing, in addition, bi or multimodal distributions. Even in the best conditions tested (entry 4), the polymeric material (60%) displays a multimodal distribution, with an unacceptable large quantity of oligomers (28%).

Comparing the behaviour of monomers 1 and 2 towards their polymerisation with these Rh(I)-based binary systems, a completely unexpected reactivity reversal was found. In fact, at the beginning of this work, calixarene 2 was thought as a much simpler candidate for the production of a conjugated polymer for two main reasons: (1) the absence of phenolic hydroxyl groups in the lower rim, which might have led to the deactivation of the rhodium initiator in the case of 1 and (2) the apparently much more difficult spatial arrangement of the phenylacetylene pendants of compound 1 in order to properly interact with the rhodium complex. Although no clear-cut answer could be given at present, it seems that in the case of 2, the oxidative coupling of two calixarene units, giving the 1,3-diyne dimer 6 (Scheme 3), followed by further reactions with other calixarene units, eventually through the intermediacy of a Rh-hydride complex [21], giving trimers and higher oligomeric products, are somewhat favoured in comparison to a chain propagation reaction (Scheme 3).

The oxidative coupling of two calix[4]arene 2 units under a Glaser-type [33] reaction should provide the dimer compound 6. Indeed, when 2 was treated with  $\text{CuCl/TMEDA}$  (Hay modification) [34] in toluene at  $60^\circ\text{C}$  for 1.5 h, we were able to isolate the dimer 6 in 45% (Scheme 4). Its  $^1\text{H NMR}$  spectrum shows a very similar pattern to that of the monomer 2, except that the ethynylic proton resonance at 3.09 ppm is absent. The most visible differences in the FT-IR spectrum of 6 when compared with 2 are the absence of the  $\equiv\text{CH}$  stretching frequency at  $2112\text{ cm}^{-1}$  and the appearance of a very small but perceptible band at  $2217\text{ cm}^{-1}$ , which was assigned to  $-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$

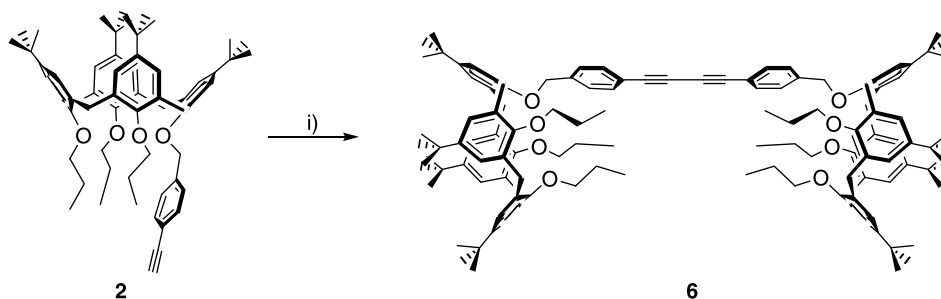


SCHEME 3 Possible pathways to the formation of dimeric (**6**), oligomeric and polymeric materials from calix[4]arene **2**, through the intermediacy of Rh(I) complexes.

stretching. Its GPC retention volume [ $M_{w(\text{GPC})} = 1624$  (PDI = 1.01),  $M_w$  of **6** is  $1776.58 \text{ g mol}^{-1}$ ] exactly matches that of the dimer obtained during the polymerisation of **2**.

Submitting the dimer **6** to the same conditions of calixarene **2** polymerisation (those of entry 3 of Table I), for 1 h, the starting material could be recovered unchanged. Adding one eq. of **2** to the reaction mixture containing **6** and, additionally,

1 mol% of  $[\text{Rh}(\text{nbd})\text{Cl}]$ , higher oligomeric products were formed in 3.5 h (the mixture stops stirring at this time due to its high viscosity) at the expenses of **2** and, probably, **6**. However, the definitive involvement of **6** in the course of the oligomerisation reactions could not be proved, since the quantification of all the intervening species by GPC analysis was not feasible with accuracy, mainly due to the low conversion attained.



SCHEME 4 Synthesis of dimer **6**: (i)  $\text{CuCl}$  (5 mol%), TMEDA (5.7 mol%), toluene,  $65^\circ\text{C}$ , 1.5 h.

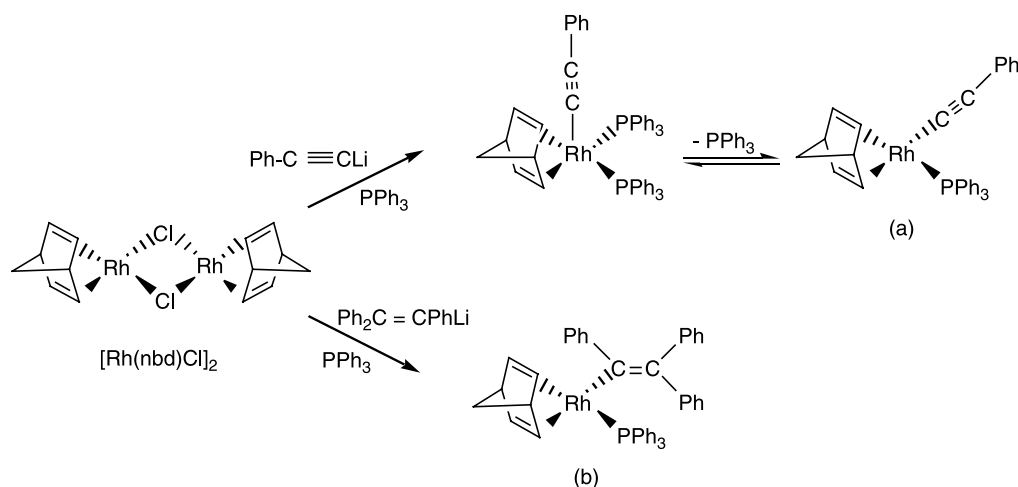


CHART 1 Catalytic systems introduced by (a) Noyori *et al.* (20) and (b) Masuda *et al.* (22) for the living polymerisations of arylacetylenes.

Assuming that with more highly active Rh(I) initiators, either the initiation step or the chain propagation reactions would occur more efficiently, we turn our attention to this type of systems.

### Living Polymerisations

The living polymerisation of monosubstituted phenylacetylenes (PAs) using Rh(I) catalysts has been accomplished essentially with two different catalytic systems. Noyori *et al.* first reported that  $\text{Rh}(\text{C}\equiv\text{CPh})(\text{nbd})(\text{PPh}_3)_2/4\text{-DMAP}$  [20] and  $[\text{Rh}(\text{nbd})\text{OMe}]_2/\text{PPh}_3/4\text{-DMAP}$  [36] systems promote the living polymerisation of PA. They showed that a tetracoordinated Rh(I) complex bearing a phenylethynyl group,  $\text{PPh}_3$  and norbornadiene ligand attached to the rhodium centre (Chart 1 (a)) was effective in PA polymerisation and that it proceeds in a living fashion with initiation efficiencies ( $I_{\text{eff}}$ ) ranging from 37 to 72% [20,21,36]. The initiator was either prepared from  $[\text{Rh}(\text{nbd})\text{Cl}]_2$ ,  $\text{PhC}\equiv\text{CLi}$  and  $\text{PPh}_3$  in  $\text{Et}_2\text{O}$ , and then isolated or formed *in situ* either from  $[\text{Rh}(\text{nbd})\text{OMe}]_2$  or a mixture of  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  and  $\text{NaOMe}$  and  $\text{PPh}_3$ , and then reacted with PA. 4-DMAP was found essential for the narrowing of polydispersity. The probable mechanisms underlying this type of polymerisations, regarding the initiation and propagation steps, were latter scrutinised [21]. As far as the initiation step is concerned, an Rh–H complex is first formed, through the reductive elimination of diphenylbutadiyne, which then adds an ethynyl moiety thus forming a Rh–vinyl complex, from which further insertion of monomeric species can occur [35].

New TCS of the type  $[\text{Rh}(\text{diene ligand})\text{Cl}]_2/(\text{Ar})_2\text{C}=\text{C}(\text{Ar})\text{Li}/\text{P}(4\text{-R-C}_6\text{H}_4)_3$  ( $\text{R}=\text{H, F, Cl}$ ) were later introduced by Masuda *et al.* [22, 37–39] (Chart 1 (b),  $\text{Ar}=\text{Ph}$  and  $\text{R}=\text{H}$ ). The rationale behind the

development of such systems is the direct formation of a Rh–vinyl bond, which was assumed as a key element for the high efficiency of the catalytic system [22] since it allows the direct insertion of ethynyl monomers into the  $\sigma$ -bound vinylic ligand, thus leading directly to the propagating species. The living nature of these systems was proved in several instances and they generally provide the most efficient ( $I_{\text{eff}}$  rounding 100%) polymerisation method so far available.

As described in the preceding section, the attempted polymerisation of calixarene **2** was not successful with the use of binary catalytic systems  $[\text{Rh}(\text{nbd})\text{Cl}]_2/\text{co-catalyst}$  ( $\text{NHET}_2$ ,  $\text{NET}_3$ , *n*-BuLi or  $\text{PPh}_3$ ). Even in the case of calixarene **1** where conjugated polymers were obtained in good yields, there is plenty of room for development of better polymerisation systems since, for instance, under our best reported [18] conditions, long reaction times are needed for high conversions and the amount of low-molecular-weight materials was still significant (*ca.* 5%), limiting, somehow, the direct use of the thus isolated polymers in several potential applications where a high purity of the materials is of utmost importance in relation to their photo/electroluminescent and magnetic properties. Therefore, we decide to study the behaviour of calixarene **1** and **2** with TCS (always prepared *in situ*), following the two conceptual approaches described above.

### Polymerisation of Calix[4]arenes 1 and 2 with TCS I

A polymerisation initiator of the type  $\text{Rh}(\text{C}\equiv\text{CPh})(\text{nbd})(\text{PPh}_3)_2$  [20, 21] was tentatively prepared *in situ* by the reaction of  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  with  $\text{PhC}\equiv\text{CLi}$  and  $\text{PPh}_3$  in toluene, using different molar ratios of  $[\text{PhC}\equiv\text{CLi}]:[\text{Rh}]$ , temperatures and periods for the ageing process of the catalytic system. Selected experiments are reported in Table II.

Under the conditions similar to those used by Noyori *et al.* [20] for the polymerisation of PA, except that an *in situ* prepared system and toluene were used in our case, calixarene **2** was polymerised in 40.5% after 1 h at 30°C. Despite the polymer yield remains low (55%) after 3 h, the total amount of low-molecular-weight materials (dimer/oligomers) was kept under 1% (entry 1, Table II). The formation of the active catalytic species seems to be directly related to the ageing period of the catalytic system. Indeed, when the PhC≡CLi solution was added to [Rh(nbd)Cl]<sub>2</sub>, containing the phosphine and, immediately following, the monomer solution is added, a lower conversion (22%, 1 h) was obtained (entry 2, Table I). Using the last procedure with enhanced molar ratios of [PhC≡CLi]:[Rh] (entries 3 and 4), similar results were obtained (conversions,  $M_n$  and PDI). Therefore, the excess of the ethynylating reagent, on its own, does not seem to have any beneficial effect on the outcome of the reaction. Raising the temperature at which the ageing period of the catalytic system is performed (from 0 to 30°C) has also no useful consequence on the formation of the active catalytic species (entry 5). Moreover, very little polymerisation seems to occur after 1 h of reaction, probably because the complete deactivation of the catalyst takes place under these conditions. Under identical conditions of the last entry, the addition of triethylamine ([NEt<sub>3</sub>]:[Rh] = 25) to [Rh(nbd)Cl]<sub>2</sub>, before PhC≡CLi has been added, seems to have a favourable action (entry 6), affording **poly 2** in 70% after 3 h, while the oligomers/dimer products are still maintained at a low level. An 85% conversion was attained for **poly 2** in 1 h, when the very same catalytic system as before was aged at 0°C for 2 h (entry 7, cf. entry 1). An identical result was obtained with calixarene **1** (entry 13), for which a conversion of 75% was achieved.

All the above experiments were carried out in the presence of catalytic amounts of phenylacetylene (Table II) during the preparation of the TCS. The rationale behind its use was that it could work in a sacrificial mode rendering the Rh-H complex, concomitantly with PhC≡C–C≡CPh, which could further insert PA and form an active vinyl-Rh complex. If things work in this way, the subsequent addition of monomer **2** will result in its direct insertion into the Rh-vinyl bond, yielding the active propagating species.

In order to test this working hypothesis, the following experiments were undertaken. In all of them, the preparation of the TCS was done in the very same way as described before for entries 1 or 7. The general trend in this series is that all the polymerisations went slower and lower conversions were achieved, in all comparable cases. For example, under the best conditions of the previous series (entry 7), the analogous experiment (entry 8) only convert 47% of calixarene **2** into the polymer after 1 h. Doubling the

molar ratio of phenylethynyllithium to Rh metal (entry 9, [PhC≡CLi]:[Rh] = 10) has no effect on the outcome of the polymerisation. Performing the polymerisation in the presence of 4-DMAP instead of NEt<sub>3</sub>, **poly 2** was obtained in only 17% (1 h, entry 10, cf. entries 8 and 1). Raising the molar ratio of NEt<sub>3</sub> to Rh (cf. entries 8 and 11), a slight improvement in the conversion was found. The importance of the role of phenylethynyllithium in the generation of the active initiator was next assessed. Preparing the catalytic system by combining [Rh(nbd)Cl]<sub>2</sub>, PhC≡CH, PPh<sub>3</sub> and NEt<sub>3</sub> (molar ratios, 1:10:10:150), under the general procedure of TCS I preparation (no PhC≡CLi was used), **poly 2** was obtained in only 3% after 1 h (entry 12); after 3 h, the yield of the polymer remains quite low (29%) and the amount of oligomeric and dimeric products totalise 8.5%. This last result confirms the significant role of the ethynylation reagent on the preparation of the active catalyst.

Some integrative comments are in order from the foregoing results: (1) the presence of catalytic amounts of phenylacetylene, in addition to phenylethynyllithium, in the catalytic system (entries 1–7) is beneficial since it both increases the apparent rate of the polymerisation of **2** and allows higher conversions; (2) whatever the particular conditions used (first or second series), the addition of NEt<sub>3</sub> to the Rh catalyst precursor seems to greatly enhance the performance of the catalytic system and (3) the formation of the active initiator is absolutely dependent on the presence of phenylethynyllithium.

Finally, it should be noted that the various catalytic systems under study should have some living character since the  $M_n$  of **poly 2** generally increases with the monomer conversion, albeit the broad MWD appears to indicate that irreversible chain breaking reactions (by transfer or termination) occur at a reasonable extent.

### Polymerisation of Calix[4]arenes **1** and **2** with TCS II

A remarkable effect was witnessed when calix[4]arene **1** was polymerised by a TCS prepared *in situ* from [Rh(nbd)Cl]<sub>2</sub>, 1,1-diphenyl-2-phenylvinyl lithium and PPh<sub>3</sub> in toluene at 30°C. Indeed, under the best conditions, the polymerisation yield was almost quantitative (entries 1–2 and 5, GPC analysis) and the amount of dimeric and oligomeric products was kept at a minimum. Representative examples are listed in Table III.

A brief comparison of these results with those previously reported [18] and others obtained in the course of the present work using the TCS I (entry 13, Table II) undoubtedly reveals that very high initiation and propagation rates are associated with the performance of this TCS. All the experiments proceed in homogeneous phase, affording in all instances conjugated polymers that are freely soluble

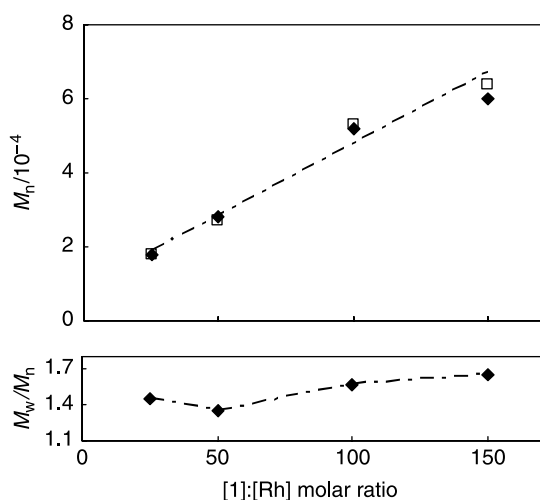


FIGURE 1  $M_n$  and  $M_w/M_n$  of **poly 1** versus [1]:[Rh] molar ratios plots in the polymerisation of calix[4]arene **1** by the TCS II. (a) □, **poly 1** in the crude reaction mixture, (b) ◆, isolated **poly 1**.

in nonprotic organic solvents (e.g.  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , toluene, THF, hexane). Looking at the results shown in Table III, one immediately sees that, as the [1]:[Rh] molar ratio is incremented, the overall conversion decreases, as well as the polymer yield and the amount of oligomeric and dimeric products increase. The higher viscosity developed in some polymerisation mixtures (entries 3 and, particularly, 4) may explain the lower conversions achieved in these cases since the bimolecular reaction between the propagating chain and the monomer is more strongly limited, inhibiting the propagation steps to proceed normally. These could also explain the observed broadening of polydispersity in the corresponding polymers (entries 3–4).

Using different monomer-to-catalyst molar ratios (25:1, 50:1, 100:1 and 150:1), a linear relationship could be obtained between the number average molecular weight ( $M_{n(\text{GPC})}$ ) of **poly 1** and the [1]:[Rh] feed ratio (Fig. 1). The proportional increase in  $M_n$  of **poly 1** with the feed ratio indicates that the initiation efficiency should be high and the propagating polymeric chains did not change their concentration during the course of the polymerisation; therefore no chain breaking (transfer or termination) seems to occur to a major extent. This result clearly evidences that the polymerisation of **1** has proceeded in a living fashion.

This system was next applied to the polymerisation of calix[4]arene **2**. The results are shown in Table IV.

Excellent results were again obtained with TCS II. The same general trends observed in the polymerisation of **1** also apply to this monosubstituted analogue. For example, a very fast polymerisation occurs within 1 h, obtaining a very good isolated yield of **poly 2** in (82.5%; entry 5), with practically no low-molecular-weight products and a quite narrow

polydispersity. All the conjugated polymers obtained are soluble in common nonprotic organic solvents. As before, when higher [2]:[Rh] molar ratios were used (entries 3 and 4), the polymerisation mixtures turned quite viscous after 40 min, completely preventing the stirring of the contents. As a result, these reactions did not go to completion and the polymer yields decrease correspondingly. In addition, the polydispersity of the isolated polymeric materials are much broader, probably by some reasons explained above for **poly 1**. Unfortunately, the anomalous behaviour of these two last experiments precluded the gathering of more detailed data on the living nature of the polymerisation.

### Characterisation of Poly 1 and Poly 2

Structural analysis of **poly 1** and **poly 2** was assessed by  $^1\text{H}$  NMR, UV–Vis, FT-IR and microanalysis. The most characteristic feature of the FT-IR spectra of **poly 1** and **poly 2** is that the ethynylic stretching vibrations that appeared at 3302–3257 and 3309–3270  $\text{cm}^{-1}$  ( $\equiv\text{CH}$ , for **1** and **2**, respectively) and 2106 and 2112  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{C}$ , for **1** and **2**, respectively), are all missing. The conjugated nature of **poly 1** and **poly 2** may be readily accessed through their UV–Vis spectra. The  $\pi \rightarrow \pi^*$  transitions of the polymer backbone in the case of **poly 1** showed an absorption band peaking at 400 nm ( $\epsilon_{\text{max}} = 1.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), whereas for **poly 2** the maximum appeared at a longer wavelength (466 nm;  $\epsilon_{\text{max}} = 8.3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ), probably reflecting an extended conjugation length of the polymer chain.

The  $^1\text{H}$  NMR spectra of **poly 1** and **poly 2** show very broad signals, precluding a detailed analysis of the polymer's structure, in particular the one concerning to the stereochemistry of the main chain. However, in both polymers, a broad, although perceptible, resonance appeared at *ca.* 5.9 ppm, which might indicate that a *cis*-transoidal configuration of the polyene chain has been attained, as should be expected from this type of catalyst.

### CONCLUSIONS

Living polymerisation methodologies based on Rh(I) TCS were successfully applied to the polymerisation of mono and difunctional phenylethynylcalix[4]arene compounds **1** and **2**. It was demonstrated that by the use of two TCS, prepared *in situ* from  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  and appropriate co-catalysts, very good to excellent yields of **poly 1** and **poly 2** were obtained, being the amount of dimeric and oligomeric products formed negligible, thus fulfilling one of the goals of this work. Moreover, a controlled growth of the polymeric chains was achieved with either calix[4]arene monomers (**1** and **2**), which allowed the synthesis of calix[4]arene conjugated

polymers with tailored  $M_n$  and good to fair narrow MWD.

The exploitation of the conceptual and experimental work here described will potentiate new challenging opportunities to design and create new supramolecular systems based on calixarene building blocks for sensing and actuation devices.

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