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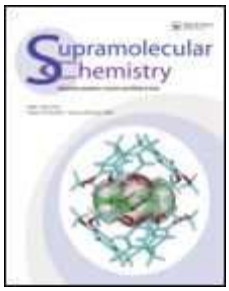

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Studies Toward the Living Polymerization of Phenylethynyl-Calix[4]arene Compounds with Rh-based Ternary Catalytic Systems

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

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ABSTRACT

The living polymerization 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: (a) Rh(C≡CPh)(norbornadiene)(PPh_3) and (b) Rh(C(Ph)C=CPh_2)(norbornadiene)(PPh_3). 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_3 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 polymerization 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 polymerization has been proved. For instance, in the case of calix[4]arene **1**, the M_n of the

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polymer obtained at high monomer conversion, increased proportionally with the [**1**]:[Rh] molar ratio in the feed, keeping $[\mathbf{1}]_o$ constant, thus showing that irreversible chain transfer or termination reactions did not occur to a major extent. Under the most favorable 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 Polymerization, Rhodium, Transition-Metal Catalyst, Dimerization.

INTRODUCTION

The ability of conjugated polymers, incorporating macrocyclic receptors within their structure, to behave as specific chemical and biological sensors has been recognized.[1-8] The sensory chemistry developed within these systems relies in 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 polymers-based sensors, as compared to those builded-up from single receptor molecules, is based in 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 (*eg.* crown and aza-crown ethers,[11] cyclodextrins[12,13] and calixarenes[7,14]) have been used for this purpose. However, and 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 mono substituted derivative of calix[4]arene, possessing a diiodo

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functionality, was copolymerized with a 1,4-diethynylphenyl compound, producing a poly(phenylene ethynylene) type copolymer (M_n=14000; PDI=1.8).[7] Two other reports, also by the group of Swager, focus on the use of polythiophene[14] and poly(phenylene bithiophene)[16] type 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 polymerization with appropriate difunctional compounds. In the former case, the M_n of the polymers (two examples) range from 22000-47000 gmol^{-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 meanwhile developed. Although not conjugated polymers, 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 polymerize. None of the correspondent structures in the cone conformation yield any polymer. Instead, oligomers were formed. Besides, the polymerization 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 functionalizable preformed conjugated polymer, we have favored the way in which the polymer is synthesized directly from the calixarene-containing monomeric units. Our synthetic approach to this type of systems, involving the

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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 polymerization method to a monosubstituted calix[4]arene analog (**2**), huge amounts of oligomeric materials were retrieved or low polymerization conversions were obtained. Even in the case of calix[4]arene **1**, the polymerization is slow and, above all, neither the molecular weight of the polymer nor its molecular weight distribution (MWD) were, in any event, controlled. Thus, it seemed to us that better polymerization 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 bellow.

EXPERIMENTAL

Materials and Methods. Melting points were measured in sealed capillaries on a Büchi 530 apparatus and are reported uncorrected. The melting temperatures of the monomers were determined by differential scanning calorimetry (DSC) on a Netzsch Luxx STA 409 PC, using a heating rate of 7ºC/min under nitrogen. Infrared spectra (FT-IR) were measured on a Bruker Vertex 70 as KBr pellets (transmission mode) at a resolution of 2 cm^{-1}. ^{1}H NMR and H-decoupled ^{13}C NMR were recorded on a Brüker ARX 400 spectrometer (^{1}H, 400 MHz; ^{13}C, 100 MHz) and reported chemical shifts (δ/ppm) are internally referenced to tetramethylsilane (^{1}H) and $CD_2Cl_2/CDCl_3$ (^{13}C; 53.8 and 77.0 ppm relative to Me_4Si); *J* values are given in Hz. 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 ionization (EI, 10 eV) at ~300ºC)

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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 5.0×10^{-5}M in $CHCl_3$. Gel permeation chromatography (GPC) analysis 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 PSS SDV columns (10^3 and 10^5 Å) and THF as eluent at 35ºC. Calibration was done with monodisperse polystyrene standards. The polymeric, oligomeric and dimeric contents of the polymerization 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 polymerization 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 µm) silica-gel. Pressure-rated reaction vials with PTFE-silicon caps were used for the Sonogasira couplings performed at 120ºC.

Calix[4]arenes **1**[18] and **3**[19] were synthesized according to reported methods and characterized by FT-IR, ^{1}H NMR and microanalysis. 4-Iodobenzyl bromide (95%, Aldrich), (bicyclo[2.2.1]hepta-2,5-diene)chloro-rhodium(I) dimer ([Rh(norbornadiene)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, 1.6M and 2.5M solution in hexanes, Aldrich), bromotriphenylethylene (98%, Acros) and *N,N,N',N'*-tetramethylethylene-diamine (TMEDA, 99%, Aldrich) were used as received. Triphenylphosphine (98%, Merck) was recrystallized from hexane, diethylamine (99%, Acros

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Organics) and triethylamine (99%, Riedel-de-Haën), were previous dried from CaH_2 and distilled under N_2 and stored over molecular sieves until use. Phenylacetylene (98%, Aldrich) was pre-dried with CaH_2 and distilled from CaH_2 under N_2 just before use. All other reagents and solvents were reagent grade and were purified and dried by standard methods. Organic extracts were dried over anhydrous magnesium sulfate.

Synthesis of calix[4]arene monomers

5,11,17,23-tetrakis(1,1-dimethylethyl)-25-(4-iodobenzyloxy)-26,27,28-tripropyloxycalix[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 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 24h, the TLC control ($CHCl_3$: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 $CHCl_3$ (3x25 mL). The organic extracts were combined and the solvent removed. After vacuum drying, the residue obtained was chromatographed ($CHCl_3$:hexane; 1:2), yielding 2.06 g (80.5%) of a colorless solid which on recrystallization (CH_2Cl_2:MeOH) furnished colorless crystals; mp 149-151ºC; ν_{max}/cm^{-1} 3042, 2963, 2872, 1602, 1590, 1484, 1205, 1008, 868, 802; δ_H/ppm ($CDCl_3$) 0.81 (6H, t, -CH_2-C$\underline{H}_3$, *J* 7.4), 0.96 (9H, s, C(C$\underline{H}_3$)$_3$), 0.99 (9H, s, C(C$\underline{H}_3$)$_3$), 1.02 (3H, t, -CH_2-C$\underline{H}_3$, *J* 7.4), 1.18 (18H, s, C(C$\underline{H}_3$)$_3$), 1.86 (4H, m, -C$\underline{H}_2$-CH_3), 1.98 (2H, m, -C$\underline{H}_2$-CH_3, *J* 7.4), 3.07 (2H, d, ArC$\underline{H}_2$Ar, *J* 12.5), 3.09 (2H, d, ArC$\underline{H}_2$Ar, *J* 12.5), 3.75 (6H, m, -O-C$\underline{H}_2$-CH_2-CH_3), 4.34 (2H, d, ArC$\underline{H}_2$Ar, *J* 13.1), 4.37 (2H, d, ArC$\underline{H}_2$Ar, *J* 13.1), 4.77 (2H, s, ArOC$\underline{H}_2$Ar), 6.62 (2H, s, Ar$\underline{H}$), 6.66 (2H, s, Ar$\underline{H}$), 6.90 (4H, s, Ar$\underline{H}$), 7.24 and 7.71 (2H each, d each, I-Ar$\underline{H}$, *J* 8.1); δ_C/ppm (CD_2Cl_2) 10.2, 10.7 (2 -O-CH_2-CH_2-$\underline{C}H_3$, ratio 2:1), 23.55, 23.9 (2 -O-CH_2-$\underline{C}H_2$-CH_3, ratio 2:1), 31.4, 31.55, 31.75 (C($\underline{C}H_3$)$_3$ and -$\underline{C}H_2$), 34.0, 34.1, 34.2

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(3 $\underline{C}(CH_3)_3$, ratio 2:1:1), 77.1, 77.2, 77.5 (2 -O-$\underline{C}H_2$-CH_2-CH_3 and -O-$\underline{C}H_2$-Ar), 93.8 (-Ar$\underline{C}$-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 (Ar$\underline{C}$ and Ar$\underline{C}$-H) [fewer carbon signals than expected in the region 31-32 ppm (3 $C(\underline{C}H_3)_3$ and 2 bridged CH_2) due to accidental isochrony]. HR-MS (FT-ICR-MS, EI) m/z: 990.5002 (M^+, $C_{60}H_{79}IO_4$ requires 990.5018). Anal. Calcd. for $C_{60}H_{79}IO_4$: 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-tripropyloxycalix[4]arene (5). Procedure A: To a stirred solution of **4** (200 mg, 0.202 mmol) in 0.8 mL of dry NEt_3 under argon at rt was successively added $Pd(OAc)_2$ (1.2 mg, 5.1 μmol), CuI (1.92 mg, 10.1 μmol) and PPh_3 (2.65 mg, 10.1 μmol). The clear pale yellow solution that results was kept at rt for 1h with stirring. After that time, $(CH_3)_3SiC{\equiv}CH$ (34 μL, 0.242 mmol) was added to the slightly turbid yellow-greenish solution that meanwhile has been formed. The reaction mixture, which has acquired a dark brown color, was then stirred at 50ºC under an inert atmosphere. After 24h, TLC control (CH_2Cl_2:hexane; 1:4; 2 elutions) indicated an essentially complete reaction. The contents of the flask were filtered and the solids washed with CH_2Cl_2. The filtrate was evaporated to dryness in a rotary evaporator. The dark brown residue was taken in CH_2Cl_2 and washed twice with a saturated NH_4Cl solution. The organic extract was dried, the solvent removed and the residue was dried under vacuum, yielding 166.5 mg of a crude product in almost pure state (TLC, ^{1}H NMR). Flash chromatography (CH_2Cl_2:hexane; 1:3) furnished 80.2% of **5** as a colorless solid. Colorless crystals were obtained upon recrystallization from CH_2Cl_2:MeOH; mp 198-199ºC; ν_{max}/cm^{-1} 3033, 2963, 2875, 2158, 1603, 1581, 1480, 1249, 1205, 1123, 1010, 868, 842, 760; δ_H/ppm ($CDCl_3$) 0.27 (9H, s, $Si(C\underline{H}_3)_3$), 0.84 (6H, t, -CH_2-$C\underline{H}_3$, *J* 7.5), 0.97 (9H, s, $C(C\underline{H}_3)_3$), 0.99 (9H, s, $C(C\underline{H}_3)_3$), 1.02 (3H, t, -CH_2-$C\underline{H}_3$, *J* 7.5), 1.18 (18H, s, $C(C\underline{H}_3)_3$), 1.89 (4H, m, -$C\underline{H}_2$-CH_3), 2.00 (2H, m, -$C\underline{H}_2$-CH_3, *J* 7.5), 3.04 (2H, d, Ar$C\underline{H}_2$Ar, *J* 12.5), 3.10 (2H, d, Ar$C\underline{H}_2$Ar, *J* 12.5), 3.76 (6H, m, -O-$C\underline{H}_2$-CH_2-

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CH_3), 4.33 (2H, d, ArC$\underline{H}_2$Ar, *J* 12.5), 4.38 (2H, d, ArC$\underline{H}_2$Ar, *J* 12.5), 4.82 (2H, s, ArOC$\underline{H}_2$Ar), 6.63 (2H, s, Ar$\underline{H}$), 6.65 (2H, s, Ar$\underline{H}$), 6.89 (4H, s, Ar$\underline{H}$), 7.39 and 7.46 (2H each, d each, $(CH_3)_3SiC{\equiv}C$-Ar$\underline{H}$, *J* 8.0); δ_C/ppm (CD_2Cl_2) 0.03 (-Si($\underline{C}H_3)_3$), 10.2, 10.7 (2 -O-CH_2-CH_2-$\underline{C}H_3$, ratio 2:1), 23.6, 23.9 (2 -O-CH_2-$\underline{C}H_2$-CH_3, ratio 2:1), 31.4, 31.55, 31.7 (C($\underline{C}H_3)_3$ and -$\underline{C}H_2$), 34.0, 34.1, 34.2 (3 $\underline{C}(CH_3)_3$, ratio 2:1:1), 77.2, 77.25 (shoulder), 77.5 (2 -O-$\underline{C}H_2$-CH_2-CH_3 and -O-$\underline{C}H_2$-Ar), 94.5 (Ar-$\underline{C}{\equiv}$C-Si$(CH_3)_3$), 105.4 (Ar-C$\equiv\underline{C}$-Si$(CH_3)_3$), 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 (Ar$\underline{C}$ and Ar$\underline{C}$-H) [fewer carbon signals than expected in the region 31-32 ppm (3 C($\underline{C}H_3)_3$ and 2 bridged CH_2) due to accidental isochrony]. HR-MS (FT-ICR-MS, EI) m/z: 960.6470 (M^+, $C_{65}H_{88}O_4Si$ requires 960.6446). Anal. Calcd. for $C_{65}H_{88}O_4Si.1.5H_2O$: C, 78.98; H, 9.28. Found: C, 78.68; H, 9.35. The presence of water was qualitatively confirmed in the ^{1}H NMR spectrum.

Procedure B: The previously reported procedure for the diethynylation of 1,3-bis-(4-iodobenzyloxy)-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-tripropyloxycalix[4]arene (2). Calix[4]arene **5** (585.6 mg, 0.609 mmol) was first solubilized 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 25ºC under argon. The hydrolysis was followed by TLC (CH_2Cl_2:hexane; 1:1) and FT-IR. After 22h the reaction was worked-up. The solvents were evaporated and the residual yellow mass was taken in CH_2Cl_2 (10 mL) and extracted with H_2O (10 mL). The aqueous phase was back extracted with CH_2Cl_2 (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, ^{1}H NMR). Whenever necessary, this compound was chromatographed (CH_2Cl_2:hexane; 2:1); t_m (DSC) 157.5 (onset 150.5ºC); recrystallization from

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CH_2Cl_2:MeOH furnished colorless crystals; mp 146-148ºC; ν_{max}/cm^{-1} 3309, 3270, 3033, 2963, 2871, 2112, 1603, 1583, 1481,1202, 1123, 1008, 871, 823; λ_{max}/nm (ε_{max}x10^{-3} M^{-1}cm^{-1}) 276 (4.3), 282 (4.3); δ_H/ppm ($CDCl_3$) 0.81 (6H, t, -CH_2-C$\underline{H}_3$, *J* 7.4), 0.95 (9H, s, C(C$\underline{H}_3$)$_3$), 0.98 (9H, s, C(C$\underline{H}_3$)$_3$), 1.02 (3H, t, -CH_2-C$\underline{H}_3$, *J* 7.4), 1.18 (18H, s, C(C$\underline{H}_3$)$_3$), 1.87 (4H, m, -C$\underline{H}_2$-CH_3), 1.98 (2H, m, -C$\underline{H}_2$-CH_3, *J* 7.5), 3.07 (2H, d, ArC$\underline{H}_2$Ar, *J* 12.1), 3.09 (1H, s, ≡C$\underline{H}$), 3.09 (2H, d, ArC$\underline{H}_2$Ar, *J* 12.1), 3.75 (6H, m, -O-C$\underline{H}_2$-CH_2-CH_3), 4.35 (2H, d, ArC$\underline{H}_2$Ar, *J* 12.1), 4.38 (2H, d, ArC$\underline{H}_2$Ar, *J* 12.1), 4.82 (2H, s, ArOC$\underline{H}_2$Ar), 6.61 (2H, s, Ar$\underline{H}$), 6.65 (2H, s, Ar$\underline{H}$), 6.91 (4H, s, Ar$\underline{H}$), 7.45 and 7.50 (2H each, d each, HC≡C-Ar$\underline{H}$, *J* 7.9); δ_C/ppm (CD_2Cl_2) 10.2, 10.7 (2 -O-CH_2-CH_2-$\underline{C}H_3$, ratio 2:1), 23.5, 23.9 (2 -O-CH_2-$\underline{C}H_2$-CH_3, ratio 2:1), 31.4, 31.5, 31.75 (C($\underline{C}H_3$)$_3$ and -$\underline{C}H_2$), 34.0, 34.1, 34.2 (3 $\underline{C}$(CH_3)$_3$, ratio 2:1:1), 77.2, 77.3, 77.45, 77.5 (2 -O-$\underline{C}H_2$-CH_2-CH_3, -O-$\underline{C}H_2$-Ar and Ar-C≡$\underline{C}$-H), 83.9 (Ar-$\underline{C}$≡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 (Ar$\underline{C}$ and Ar$\underline{C}$-H) [fewer carbon signals than expected in the region 30-31.5 ppm (3 C($\underline{C}H_3$)$_3$ and 2 bridged $\underline{C}H_2$) due to accidental isochrony; running the ^{13}C spectrum in $CDCl_3$, the signals corresponding to -$\underline{C}H_2$- appeared at 31.1 and 31.2 ppm]. HR-MS (FT-ICR-MS, EI) m/z: 888.6094 (M^+, $C_{62}H_{80}O_4$ requires 888.6051). Anal. Calcd. for $C_{62}H_{80}O_4$.0.5H_2O: C, 82.90; H, 9.09. Found: C, 83.19; H, 9.55. The presence of water was qualitatively confirmed in the ^{1}H NMR spectrum.

The removal of the Si(CH_3)$_3$ group was also accomplished with *n*-Bu_4NF/THF, at 25ºC for 30 min-1h, in the same manner as described before for the bis-trimethylsilylethynyl derivative of calix[4]arene **1**.[18]

Biscalix[4]arene 6. To a colorless solution of compound **2** (50 mg, 56μmol) in dry toluene (560 μL) at rt it was added copper(I) chloride (0.29 mg, 2.8 μmol), under stirring. The solution turned yellow and then gradually to blue-greenish with turbidity. Immediately following, TMEDA

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(0.5 μL, 3.2 μmol) was added and the suspension introduced in a pre-heated bath at 60ºC for 1.5h. The contents were evaporated in a rotary evaporator and the residue taken in CH_2Cl_2 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 ($CHCl_3$:hexane; 1:1)]. In order to remove possible copper compounds, the solid was redissolved in CH_2Cl_2 and washed successively with 0.1 M $NaHSO_3$, 10% aq. NH_4SCN and water. After drying the organic extract, solvent evaporation and drying in vacuum, compound **6** was obtained in 45.2% as an almost colorless solid; trituration with MeOH furnished a colorless solid; mp 174-176ºC; ν_{max}/cm^{-1} 3036, 2960, 2875, 1604, 1583, 1482, 1202, 1122, 1009, 870, 820; λ_{max}/nm (ε_{max}x10^{-5} M^{-1}cm^{-1}) 298 (3.6), 316 (4.9), 338 (4.3); δ_H/ppm ($CDCl_3$) 0.82 (12H, t, -CH_2-C$\underline{H}_3$, *J* 7.5), 0.96 (18H, s, C(C$\underline{H}_3$)$_3$), 0.995 (18H, s, C(C$\underline{H}_3$)$_3$), 1.02 (6H, t, -CH_2-C$\underline{H}_3$, *J* 7.5), 1.18 (36H, s, C(C$\underline{H}_3$)$_3$), 1.88 (8H, m, -C$\underline{H}_2$-CH_3), 1.98 (4H, m, -C$\underline{H}_2$-CH_3, *J* 7.5), 3.08 (4H, d, ArC$\underline{H}_2$Ar, *J* 12.4), 3.10 (4H, d, ArC$\underline{H}_2$Ar, *J* 12.4), 3.75 (12H, m, -O-C$\underline{H}_2$-CH_2-CH_3), 4.36 (4H, d, ArC$\underline{H}_2$Ar, *J* 12.1), 4.38 (4H, d, ArC$\underline{H}_2$Ar, *J* 12.1), 4.83 (4H, s, ArOC$\underline{H}_2$Ar), 6.62 (4H, s, Ar$\underline{H}$), 6.66 (4H, s, Ar$\underline{H}$), 6.90 (8H, s, Ar$\underline{H}$), 7.47 and 7.55 (4H each, d each, Ar$\underline{H}$-C≡C-C≡C-Ar$\underline{H}$, *J* 8.0); δ_C/ppm (CD_2Cl_2) 10.2, 10.7 (2 -O-CH_2-CH_2-$\underline{C}H_3$, ratio 2:1), 23.6, 23.9 (2 -O-CH_2-$\underline{C}H_2$-CH_3, ratio 2:1), 31.4, 31.5, 31.7 (C($\underline{C}H_3$)$_3$ and -$\underline{C}H_2$), 34.0, 34.1, 34.2 (3 $\underline{C}(CH_3)_3$, ratio 2:1:1), 74.15, 77.2, 77.5 (-O-$\underline{C}H_2$-CH_2-CH_3, -O-$\underline{C}H_2$-Ar and Ar-C≡$\underline{C}$-$\underline{C}$≡CAr), 82.0 (Ar-$\underline{C}$≡C-C≡$\underline{C}$Ar), 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 (Ar$\underline{C}$ and Ar$\underline{C}$-H) [fewer carbon signals than expected in the region 31-32 ppm (3 C($\underline{C}H_3$)$_3$ and 2 bridged $\underline{C}H_2$), 70-80 ppm (2 -O$\underline{C}H_2CH_2CH_3$, -O$\underline{C}H_2$-Ar and Ar-C≡$\underline{C}$-$\underline{C}$≡C-Ar) and 133-134 ppm (2 Ar$\underline{C}$) due to accidental isochrony; running the ^{13}C spectrum in $CDCl_3$, the signals pertaining to -$\underline{C}H_2$- appeared at 31.4 and 31.5 ppm and those of Ar$\underline{C}$ at 133.40 and 133.45 ppm]. HR-MS (ESI-FT-ICR-MS) m/z: 1798.18335 ([M-Na]$^+$,

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$C_{124}H_{158}O_8Na$ requires 1798.1849). Anal. Calcd. for $C_{124}H_{158}O_8.H_2O$: C, 82.99; H, 8.99. Found: C, 82.87; H, 9.57. The presence of water was qualitatively confirmed in the ^{1}H NMR spectrum.

General procedure for the polymerization of calix[4]arene 2 using binary catalyst systems.[18] All the polymerizations were carried out in septum-sealed dry glass vials under an argon atmosphere. To a solution containing 0.104 mg (0.225 µmol) of $[Rh(nbd)Cl]_2$ in dry THF (16 µl) was added 0.236 mg (0.9 µmol) of PPh_3. The yellow solution was deaerated with argon and the tube sealed. After a stirring period of 0.5h at 30ºC, an argon-deaerated solution of 10.0 mg (11.2 µmol) of monomer **2** in dry THF (40 µl) was added through syringe under argon. The mixture was then stirred at 30ºC for a certain time, progressively acquiring an intense orange/reddish color. The polymerization mixture was quenched with a large excess of acetic acid (*ca.* 200 mol equiv. of Rh) and stirred for 20-30 min. 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 65ºC. The above procedure refers to the preparation of **poly 2** under the conditions of entry 1, Table 1 (see Results and Discussion Section). Other conditions employed for the polymerization of **2** are to be found in that table.

General procedure for the polymerization of calix[4]arene 1 and 2 using ternary catalyst systems (TCS) 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 (35µl, 0.313mmol) in dry toluene (350µl) was placed in a septum-sealed tube under argon and cooled in an ice-bath. A cooled *n*-BuLi solution (2.5M in hexane; 126µl, 0.313mmol, in 350µl of dry toluene) was then added dropwise through a syringe and the light-yellow solution stirred at 0ºC for 15min.

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$[Rh(nbd)Cl]_2$ (78μg, 0.17μmol), triphenylphosphine (0.44mg, 1.7μmol) and 4-DMAP (0.1mg, 0.85μmol) were placed in another septum-sealed tube under argon and dry toluene (45μl) was added with a syringe. The yellow solution was stirred for 15min at rt and then cooled to -15ºC. The toluene solution of phenylethynyllithium (4μl) was added with a syringe. The catalyst mixture was stirred at -15ºC for 15min and then allowed to rise to 0ºC and stirred for 2h at this temperature, resulting in a pale yellow solution.

The above procedure refers to the conditions of entry 10, Table 2. Other diverse conditions are reported in Table 2.

2. Polymerization procedure of calix[4]arenes **1** or **2** with TCS I. A solution of monomer **2** (15mg, 16.9μmol) in dry toluene (120μl), contained in a septum-sealed tube under argon, was added dropwise via syringe to the initiator solution meanwhile prepared. Stirring was continued for a certain time (see Table 2) at 30ºC. During that period, the reaction mixture progressively acquired an orange/deep-orange/reddish color, depending on the extension of the polymerization. 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 polymerization 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 (67mg, 0.2mmol) in dry toluene (1ml) contained in a septum-sealed tube under argon was cooled in an ice-bath. A cooled *n*-BuLi solution (1.6M in hexane; 127μl, 0.2mmol) was then added dropwise through a syringe. The resulting clear mixture acquired an intense yellow color. A 0.1M solution of triphenylvinyllithium was made by the addition of 0.87ml of dry toluene, which was kept in an ice-

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bath until use. $[Rh(nbd)Cl]_2$ (105μg, 0.23μmol) and triphenylphosphine (0.6mg, 2.3μmol) were placed in another septum-sealed tube under argon and dry toluene (71μl) was added with a syringe. The triphenylvinyllithium solution (57μl) was then added dropwise via syringe to the catalyst solution, which immediately develop a intense yellow color, and the resulting mixture placed in a pre-heated bath at 30ºC for 30min.

2. Polymerization procedure of of calix[4]arenes **1** or **2** with TCS II. The monomer **1** (20mg, 22.8μmol) was placed in a septum-sealed tube under argon and a solution made by the addition of dry toluene (100μl) at rt. This solution was added dropwise via syringe to the initiator solution meanwhile prepared, acquiring almost instantaneously an intense orange color. The polymerization mixture was then kept at 30ºC with vigorous stirring for a certain time (see Tables 3 and 4). During that time a color deepening was observed as well as a gradual increase in the viscosity of the reaction. After the appropriate time, the polymerization mixture was quenched with a large excess of acetic acid (200 mol equiv. of Rh), stirred for 20-30 min, and an aliquot withdrawn for 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 65ºC. The composition of the solids thus obtained was subsequently evaluated by GPC.

The above procedure refers to the preparation of **poly 1** under the conditions of entries 1-5 of Table 3. Identical procedure was used for the polymerization of calix[4]arene **2** (Table 4). In this case, the polymerization solution acquired a reddish/brown color 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; ν_{max}/cm^{-1} 3509, 3394, 3050, 3029, 2961, 2872, 1601, 1486, 1206, 1125, 1002, 875, 819; λ_{max}/nm (ε_{max}x10^{-3} M^{-1}cm^{-1}) 280 (400), 400 (13) cutoff 525; δ_H/ppm 0.94 (b s, C(C$\underline{H}_3$)$_3$), 1.26 (b s, C(C$\underline{H}_3$)$_3$), 2.8-3.6 (b m, ArC$\underline{H}_2$Ar), 3.8-5.3 (b m,

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ArC$\underline{H}_2$Ar, ArOC$\underline{H}_2$Ar), 5.9 (b s, -C$\underline{H}$=C-), 6.4-7.2 (b m, Ar$\underline{H}$), 7.2-7.6 (b m, -CH=C-Ar$\underline{H}$). Anal. Calcd. for $(C_{62}H_{68}O_4)_n$: C, 84.89; H, 7.81. Found: C, 84.12; H, 7.99.

Poly 2. Obtained in 78.5% as an orange solid; ν_{max}/cm^{-1} 3046, 3025, 2961, 2871, 1605, 1584, 1482, 1202, 1125, 1011, 870, 815; λ_{max}/nm (ε_{max}x10^{-3} M^{-1}cm^{-1}) 276 (210), 466 (8.3) cutoff 580; δ_H/ppm 0.8 (b m, -CH$_2$-C$\underline{H}_3$, C(C$\underline{H}_3$)$_3$), 1.25 (b s, C(C$\underline{H}_3$)$_3$), 1.8 (b m, -C$\underline{H}_2$-CH$_3$), 3.1 (b m, ArC$\underline{H}_2$Ar), 3.4-3.9 (b m, -O-C$\underline{H}_2$-CH$_2$-CH$_3$), 4.0-4.9 (b m, ArC$\underline{H}_2$Ar, ArOC$\underline{H}_2$Ar), 5.9 (b s, -C$\underline{H}$=C-), 6.5 (b m, Ar$\underline{H}$), 7.0 (b m Ar$\underline{H}$), 7.2-7.6 (b m, -CH=C-Ar$\underline{H}$). Anal. Calcd. for $(C_{62}H_{80}O_4)_n$: 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).

Scheme 1

Derivatization of the parent calix[4]arene **3** with 4-iodobenzyl bromide in THF, using NaH as base, afforded the intermediate iodo compound **4** in good yield (80.5%). The four sets of doublets appearing in the ^{1}H NMR spectrum at 3.07, 3.09 and 4.34, 4.37 ppm, 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)$_2$ was used as the Pd(0) source, CuI as co-catalyst and NEt$_3$ as 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$_2$[PPh$_3$]$_2$/CuI/NHEt$_2$ in THF at 120ºC in much shorter reaction times. FT-IR spectrum of **5** showed a sharp carbon triple bond stretching frequency at 2158 cm^{-1} and the characteristic

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frequencies of the $Si(CH_3)_3$ group at 1249, 868, 842 and 760 cm^{-1}, 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_{exo}-H_{endo})~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_2CO_3/MeOH/THF, 24h, 25ºC), yielding the ethynyl compound **2** in 86%. The removal of the $Si(CH_3)_3$ group could also be done by the use of (n-butyl)$_4$NF in THF, resulting in faster reactions (0.5-1h, 25ºC) and also good isolated yields. The new formed triple bond derivative showed its C≡C stretching vibration at 2112 cm^{-1}, with a much lower intensity when compared to **5**, and that of the ≡C-H appeared splitted in two bands peaking at 3309 and 3270 cm^{-1}. 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 polymerizations

Rhodium(diene) complexes (either neutral or cationic) are known as outstanding catalysts for the polymerization 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 through alcohols, amines and even water) in these polymerizations, a wide range of monomers carrying a diversity of functional groups are highly compatible with this catalyst. In particular, Rh(I)-based catalysts efficiently polymerize phenylacetylene (PA) and many of its ring

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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 the bifunctional calix[4]arene **1**, in its cone conformation, was preferentially polymerized with a binary catalytic system comprising $[Rh(nbd)Cl]_2$ and triphenylphosphine (as the sole additive) in THF at 30ºC. High conversions and good isolated yields of the corresponding conjugated polymer **poly 1** (Scheme 2)[32] were obtained under these conditions (M_n=8.8x10^4; 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 ($CHCl_3$ or toluene) or other co-catalysts ($NHEt_2$) were used instead.

Scheme 2

When the very same polymerization conditions were applied to calixarene **2** (entry 1, Table 1), the reaction stop stirring after 4.5h resulting in low monomer conversion (*ca.* 40%) with significant amounts of dimer and oligomers being formed (*ca.* 10%), in addition to 31% of polymer. The data shown in Table 1 illustrate some of the reaction parameters meanwhile changed in order to overcome the aforementioned result. The use of amines ($NHEt_2$ or NEt_3) as co-catalysts proved much worst, whatever the solvent used. In these cases (entries 2-6), oligomeric materials were normally retrieved as the major products. When $NHEt_2$ was used, the main oligomeric compound found in the polymerization 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 favored when higher diluted solutions of the monomer are used (cf. *eg.* entries 5 and 6). The nature of the amine does not appear to have any deep influence in the conversion or on the polymer yield (entries 2 and 3). The use of *n*-BuLi in conjunction with PPh_3 did not bring any improvement to the overall polymerization performance.[33]

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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%).

Table 1

Comparing the behavior of monomers **1** and **2** toward their polymerization 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: a) 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 b) 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 favored in comparison to a chain propagation reaction (Scheme 3).

Scheme 3

The oxidative coupling of two calix[4]arene **2** units under a Glaser type[34] reaction should provide the dimer compound **6**. Indeed, when **2** was treated with CuCl/TMEDA (Hay modification)[35] in toluene at 60ºC for 1.5h, we were able to isolate the dimer **6** in 45% (Scheme 4). Its ^{1}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** as compared to **2**, are the absence of the ≡CH stretching frequency at 2112 cm^{-1} and

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the appearance of a very small but perceptible band at 2217 cm^{-1}, which was assigned to -C≡C-C≡C- stretching. Its GPC retention volume [$M_{w\ (GPC)}$=1624 (PDI=1.01); M_w of **6** is 1776.58 $gmol^{-1}$] exactly matches that of the dimer obtained during the polymerization of **2**.

Scheme 4

Submitting the dimer **6** to the same conditions of calixarene **2** polymerization (those of entry 3 of Table 1), for 1h, the starting material could be recovered unchanged. Adding one equiv. of **2** to the reaction mixture containing **6** and, additionally, 1 mol% of [Rh(nbd)Cl], higher oligomeric products were formed in 3.5h (the mixture stop 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 oligomerization 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.

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

Living Polymerizations[36]

The living polymerization of monosubstituted phenylacetylenes (PAs) using Rh(I) catalysts has been accomplished essentially with two different catalytic systems. Noyori *et al.* first reported that Rh(C≡CPh)(nbd)$(PPh_3)_2$/4-DMAP[20] and $[Rh(nbd)OMe]_2/PPh_3$/4-DMAP[37] systems promote the living polymerization of PA. They showed that a tetracoordinated Rh(I) complex bearing a phenylethynyl group, PPh_3 and a norbornadiene ligand attached to the rhodium center [Chart 1, (a)] was effective in PAs polymerization and that it proceeds in a living fashion with initiation efficiencies (I_{eff}) ranging from 37% to 72%.[20,21,37] The initiator was either prepared from $[Rh(nbd)Cl]_2$, PhC≡CLi, and PPh_3 in Et_2O and then isolated or formed *in situ* either from

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[Rh(nbd)OMe]$_2$, or a mixture of [Rh(nbd)Cl]$_2$ and NaOMe, and PPh$_3$ and then reacted with PA. 4-DMAP was found essential for the narrowing of polydispersity. The probable mechanisms underlying this type of polymerizations, regarding the initiation and propagation steps, were latter scrutinized.[21] As far as the initiation step is concerned, a Rh-H complex is first formed, through the reductive elimination of diphenylbutadiyne, which then adds a ethynyl moiety thus forming a Rh-vinyl complex, from which further insertion of monomeric species can occur.

Chart 1

New ternary catalyst systems of the type [Rh(diene ligand)Cl]$_2$/(Ar)$_2$C=C(Ar)Li/P(4-R-C$_6$H$_4$)$_3$ (R=H, F, Cl), were later introduced by Masuda *et al.*[22,38-40] [Chart 1, (b); Ar=Ph and R=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 ethynylic monomers into the σ-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_{eff} rounding 100%) polymerization method so far available.

As described in the preceding section, the attempted polymerization of calixarene **2** was not successful with the use of binary catalytic systems [Rh(nbd)Cl]$_2$/co-catalyst (NHEt$_2$, NEt$_3$, *n*-BuLi or 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 polymerization 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

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we decide to study the behavior of calixarene **1** and **2** with ternary catalytic systems (always prepared *in situ*), following the two conceptual approaches described above.

Polymerization of calix[4]arenes 1 and 2 with TCS I

A polymerization initiator of the type Rh(C≡CPh)(nbd)$(PPh_3)_2$[20,21] was tentatively prepared *in situ* by the reaction of $[Rh(nbd)Cl]_2$ with PhC≡CLi and PPh_3 in toluene, using different molar ratios of [PhC≡CLi]:[Rh], temperatures and periods for the aging process of the catalytic system. Selected experiments are reported in Table 2.

Table 2

Under conditions similar to those used by Noyori *et al.*[20] for the polymerization of PA, except that an *in situ* prepared system and toluene were used in our case, calixarene **2** was polymerized in 40.5% after 1h at 30ºC. Despite the polymer yield remains low (55%) after 3h, the total amount of low molecular weight materials (dimer/oligomers) was kept under 1% (entry 1, Table 2). The formation of the active catalytic species seems to be directly related to the aging period of the catalytic system. Indeed, when the PhC≡CLi solution was added to $[Rh(nbd)Cl]_2$, containing the phosphine, and, immediately following, the monomer solution is added, a lower conversion (22%, 1h) was obtained (entry 2, Table 1). 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. Rising the temperature at which the aging period of the catalytic system is performed (from 0ºC to 30ºC) has also no useful consequence on the formation of the active catalytic species (entry 5). Moreover, very little polymerization seems to occur after 1h 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

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([NEt_3]:[Rh]=25) to [Rh(nbd)Cl]$_2$, before PhC≡CLi has been added, seems to have a favorable action (entry 6), affording **poly 2** in 70% after 3h, while the oligomers/dimer products are still maintained at a low level. An 85% conversion was attained for **poly 2** in 1h, when the very same catalytic system as before was aged at 0ºC for 2h (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 (see Table 2) during the preparation of the ternary catalytic system. 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 ternary catalytic system 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 polymerizations 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 1h. Doubling the molar ratio of phenylethynyllithium to Rh metal (entry 9; [PhC≡CLi]:[Rh]=10) has no effect on the outcome of the polymerization. Performing the polymerization in the presence of 4-DMAP instead of NEt_3, **poly 2** was obtained in only 17% (1h; entry 10; *cf.* entries 8 and 1). Raising the molar ratio of NEt_3 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]$_2$, PhC≡CH, PPh_3 and NEt_3 (molar ratios: 1:10:10:150), under the general procedure of

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TCS I preparation (no PhC≡CLi was used), **poly 2** was obtained in only 3% after 1h (entry 12); after 3h, the yield of the polymer remains quite low (29%) and the amount of oligomeric and dimeric products totalize 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: a) 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 polymerization of **2** and allows higher conversions; b) whatever the particular conditions used (first or second series), the addition of NEt_3 to the Rh catalyst precursor seems to greatly enhance the performance of the catalytic system; c) the formation of the active initiator is absolutely dependent on the presence of phenylethynyllithium.

At last 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.

Polymerization of calix[4]arenes 1 and 2 with TCS II

A remarkable effect was witnessed when calix[4]arene **1** was polymerized by a ternary catalytic system prepared *in situ* from $[Rh(nbd)Cl]_2$, 1,1-diphenyl-2-phenylvinyl lithium and PPh_3 in toluene at 30ºC. Indeed, under the best conditions, the polymerization yield was almost quantitative (entries 1-2 and 5; GPC analysis) and the amount of dimeric and oligomeric products were kept at a minimum. Representative examples are listed in Table 3.

Table 3

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 14, Table 2) undoubtedly reveals that very high

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initiation and propagation rates are associated with the performance of this ternary catalytic system. All the experiments proceed in homogeneous phase, affording in all instances conjugated polymers which are freely soluble in nonprotic organic solvents (*eg.* CH_2Cl_2, $CHCl_3$, toluene, THF and hexane). Looking at the results at Table 3, 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 polymerization 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 2-4).

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 ($M_{n(GPC)}$) of **poly 1** and the [**1**]:[Rh] feed ratio (Figure 1). The proportional increase of 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 polymerization; therefore no chain breaking (transfer or termination) seems to occur to a major extent. This result clearly evidences that the polymerization of **1** has proceeded in a living fashion.

Figure 1

This system was next applied to the polymerization of calix[4]arene **2**. Results are shown in Table 4.

Table 4

Excellent results were again obtained with TCS II. The same general trends observed in the polymerization of **1** also apply to this monosubstituted analog. For example, a very fast

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polymerization occurs within 1h, yielding **poly 2** in very good isolated yield (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 polymerization 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 the some reasons explained above for **poly 1**. Unfortunately, the anomalous behavior of these two last experiments precluded the gathering of more detailed data on the living nature of the polymerization.

Characterization of poly 1 and poly 2

Structural analysis of **poly 1** and **poly 2** was assessed by ^{1}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 cm^{-1} (≡CH, for **1** and **2**, respectively) and 2106 and 2112 cm^{-1} (C≡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 (ε_{max}=1.3x10^4 M^{-1}cm^{-1}), whereas for **poly 2** the maximum appeared at a longer wavelength (466 nm; ε_{max}=8.3x10^3 M^{-1}cm^{-1}), probably reflecting an extended conjugation length of the polymer chain.

The ^{1}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

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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 polymerization methodologies based on Rh(I) ternary catalytic systems were successfully applied to the polymerization of mono and difunctional-phenylethynylcalix[4]arene compounds **1** and **2**. It was demonstrated that by the use of two ternary catalytic systems, prepared *in situ* from $[Rh(nbd)Cl]_2$ 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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32. Although the ring-closing polymerization 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 polymerization 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.

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Chart caption

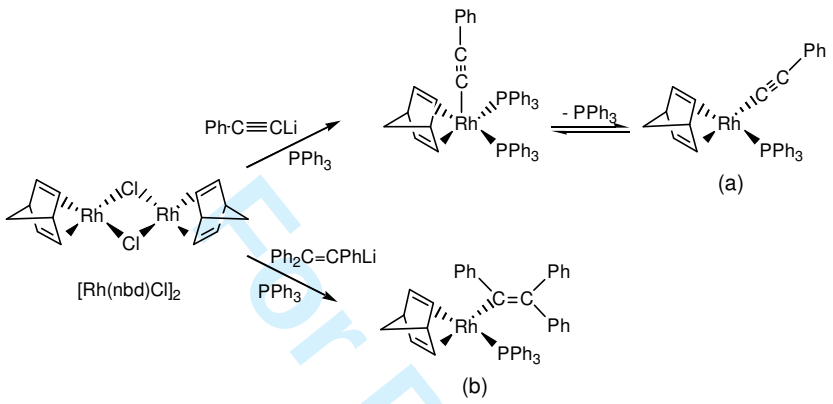

Chart 1. Catalytic systems introduced by (a) Noyori *et al.*[20] and (b) Masuda *et al.*[22] for the living polymerizations of arylacetylenes.

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Figure caption

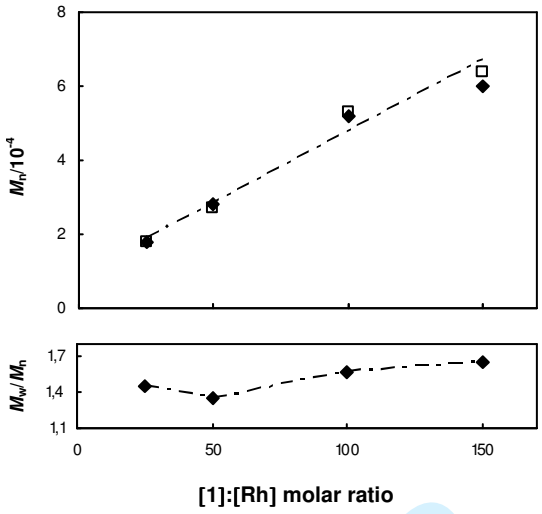

Figure 1. M_n and M_w/M_n of **poly 1** *vs* [**1**]:[Rh] molar ratios plots in the polymerization of calix[4]arene **1** by the TCS II; a) □, **poly 1** in the crude reaction mixture; b) ◆, isolated **poly 1**.

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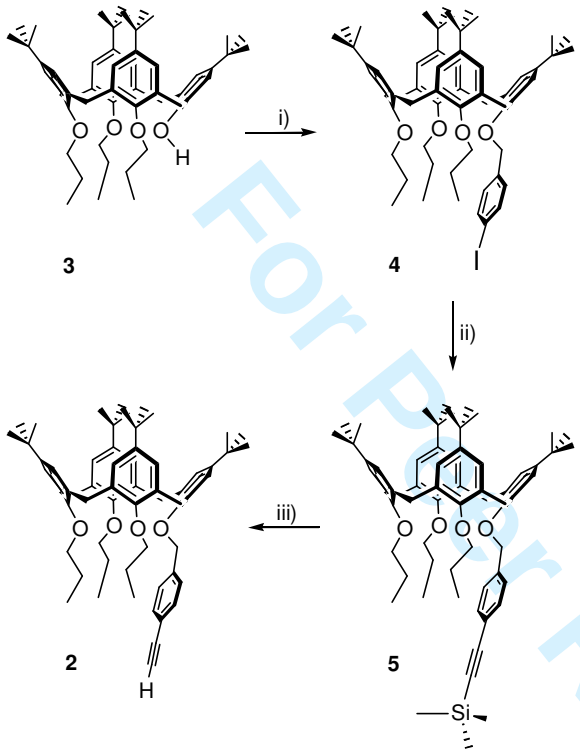
Scheme titles



Scheme 1. Synthesis of 25-(4-ethynylbenzyloxy)-26,27,28-tripropyloxycalix[4]arene **2**: i) $BrCH_2PhI$ (2.3 eq.), NaH (4.1 eq.), THF, reflux, 24h; ii) $Pd(OAc)_2$ (2.5 mol%), CuI (5 mol%), $(CH_3)_3SiC{\equiv}CH$ (1.2 eq.), PPh_3 (5 mol%), NEt_3, 50ºC, 24h; iii) K_2CO_3 (0.1 eq.), THF/MeOH, 25ºC, 22h.

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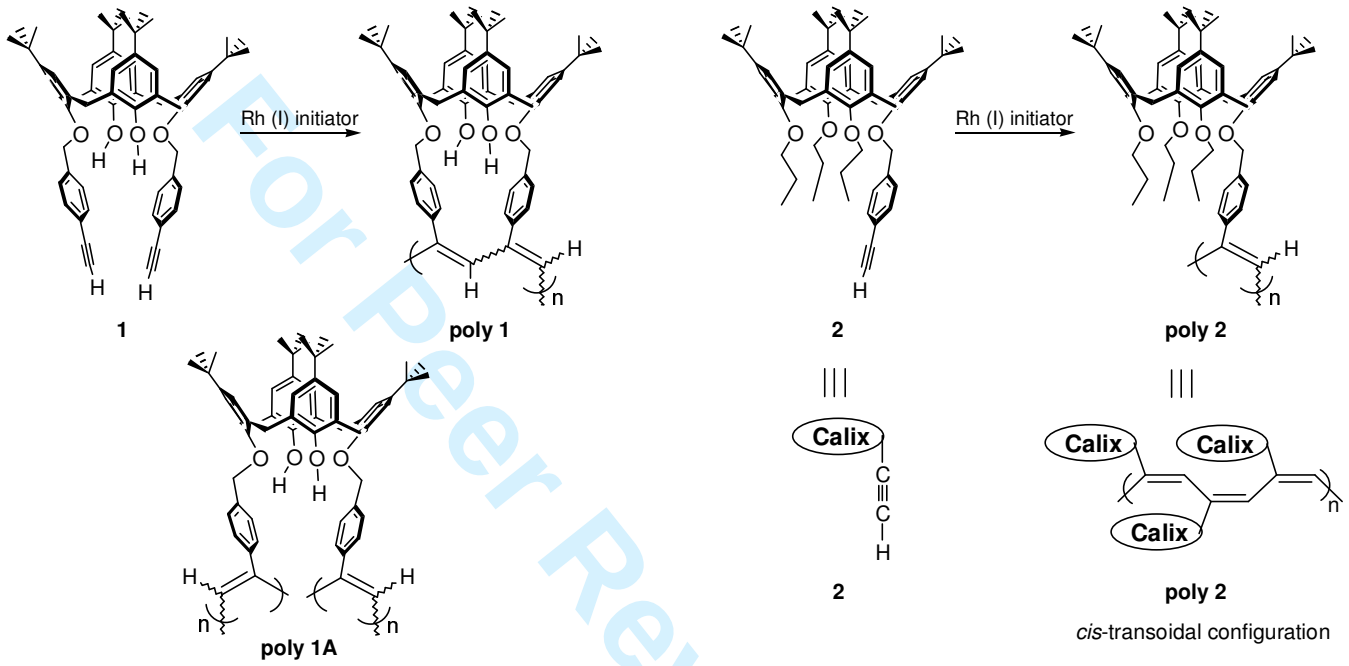
Scheme titles (cont.)



Scheme 2. Rh(I) catalyzed polymerization of calix[4]arenes **1** and **2** and the possible structures of the resulting polymers.[32]

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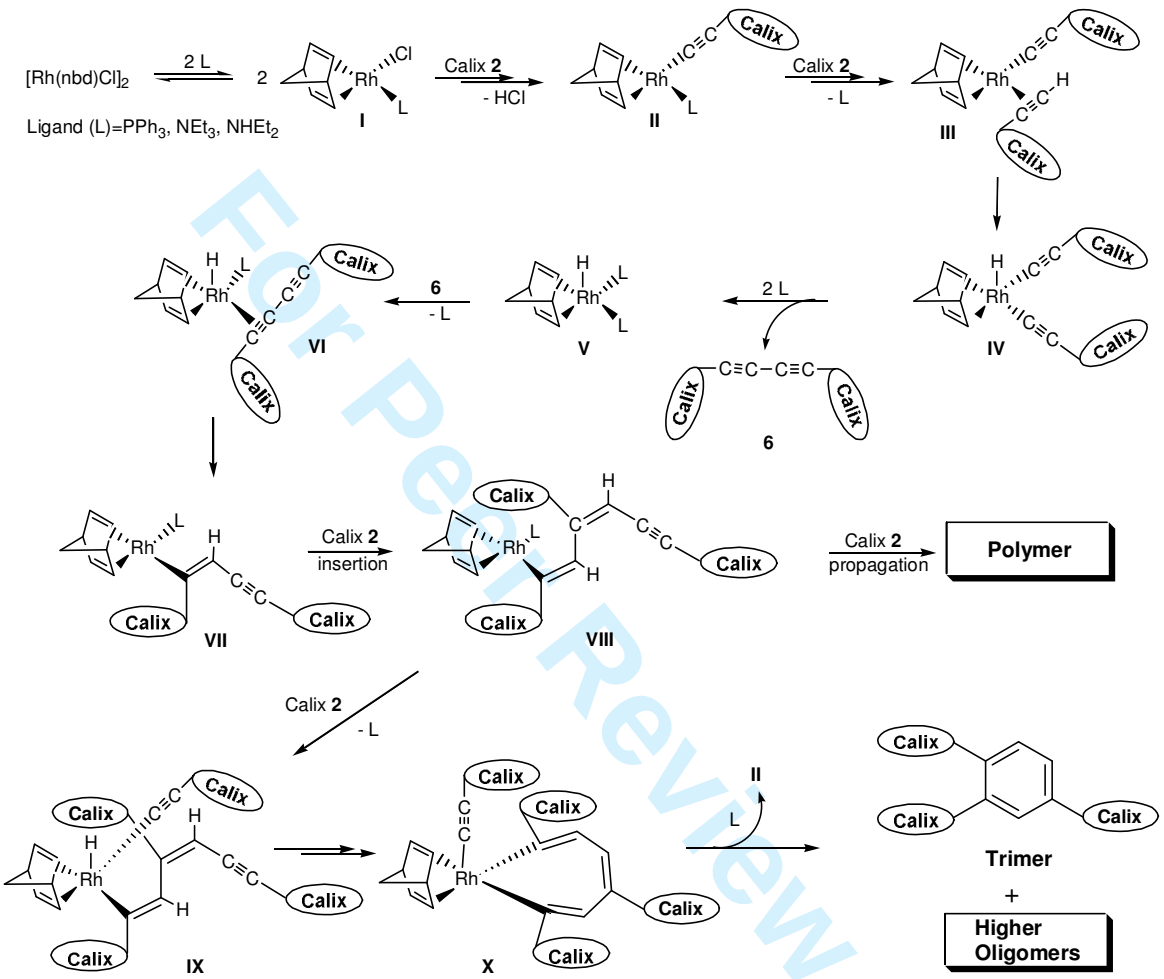
Scheme titles (cont.)



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.

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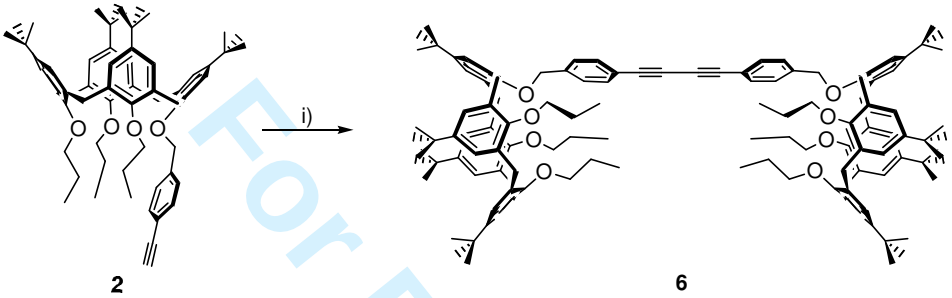

Scheme 4. Synthesis of dimer **6**: i) CuCl (5 mol%), TMEDA (5.7 mol%), toluene, 65ºC, 1.5h.

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Tables

Table 1. Rh (I) catalyzed polymerization of calix[4]arene **2** with binary catalytic systems[a,b]

Entry	Solvent	[**2**]	[**2**]:[Rh]	Co-catalyst (equiv/[Rh])	Time (h)	Conversion (%)[b]	Reaction mixture composition (%)[b]			M_nx10^{-4} (M_w/M_n)[c]
							Polymer	Oligomers	Dimer	
1	THF	0.2	25	PPh_3 (2)	4.5[d]	40.7	31.5	3.8	5.4	7.1 (2.31)
2	THF	0.05	50	$NHEt_2$ (100)	18.5[d]	48.3	1.6	41.9	4.8	6.0 (1.32)
3	THF	0.05	50	NEt_3 (100)	20[d]	66.7	2.9	57.7	6.2	- [e]
4	$CHCl_3$	0.07	25	$NHEt_2$ (25)	23	90.9	60.9	27.8	2.2	- [e]
5	$CHCl_3$	0.1	50	$NHEt_2$ (50)	6[d]	40.8	14.8	22.4	3.6	- [e]
6	$CHCl_3$	0.05	50	$NHEt_2$ (50)	24	94.1	19.2	69.6	5.7	- [e]
7	THF	0.1	50	*n*-BuLi (2.5)[f]	1	19.4	14.1	2.5	2.8	4.6 (2.51)

[a] Typical conditions: Monomer **2**, $[Rh(nbd)Cl]_2$, solvent and co-catalyst, 30ºC.[b] The degree of conversion and the composition of the polymerization mixture were evaluated by GPC.[c] The M_n and polydispersity (M_w/M_n) were determined by GPC (THF, 35ºC, polystyrene standards), and are referred to polymeric materials.[d] The reaction was quenched at this time due to its high viscosity, which had preventing adequate stirring of the contents.[e] Bimodal/multimodal distribution.[f] PPh_3 was also added ([phosphine]:[Rh]=5).

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Tables (cont.)

Table 2. Rh (I) catalyzed polymerization of calix[4]arenes **1** and **2** with ternary catalytic system I[a,b]

Entry	Monomer	[PhC≡CLi]:[Rh]	Additive (equiv/[Rh])	Time (h)	Conversion (%)[b]	Reaction mixture composition (%)[b]			M_nx10^{-4} (M_w/M_n)[c,d]
						Polymer	Oligomers	Dimer	
1	2	3.1[e]	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[e,f]	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 [e,f]	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 [e,f]	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[e,g]	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[e,g]	NEt_3 (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 [e]	NEt_3 (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_3 (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_3 (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_3 (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	-[h]	NEt_3 (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 [e]	NEt_3 (25)	1	76.8	75.0	-	1.8	8.6 (1.82)

[a] Typical conditions: [**2**]=0.1M, $[Rh(nbd)Cl]_2$/PhC≡CLi/PPh_3, [**2**]:[Rh]=50, [PPh_3]:[Rh]=5, toluene, 30ºC.[b] The degree of conversion and the composition of the polymerization mixture were evaluated by GPC.[c] Data refers to polymeric materials.[d] The M_n and polydispersity (M_w/M_n) were determined by GPC (THF, 35ºC, polystyrene standards).[e] Phenylacetylene was also present in the proportion: [PhC≡CH]:[PhC≡CLi]=0.6. [f] No aging period. [g] The catalytic system was aged at 30ºC for 2h.[h] A molar ratio of [PhC≡CH]:[Rh]=5 was used.

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Tables (cont.)

Table 3. Rh (I) catalyzed polymerization of calix[4]arene **1** with ternary catalytic system II[a,b]

Entry	[**1**]:[Rh]	Time (h)	Conversion (%)[b]	Reaction mixture composition (%)[b]			Isolated materials [b]		
				Polymer	Oligomers	Dimer	Yield (%)[c]	**Poly 1** (%)[b]	M_nx10^{-4} (M_w/M_n)[d]
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)

[a] Typical conditions: [**1**]=0.1M, $[Rh(nbd)Cl]_2/Ph_2C{=}CPhLi/PPh_3$, $[PPh_3]$:[Rh]=5, toluene, 30ºC.[b] The degree of conversion, the composition of the polymerization mixture and that of isolated materials were evaluated by GPC.[c] Gravimetrically determined yield.[d] The M_n and polydispersity (M_w/M_n) were determined by GPC (THF, 35ºC, polystyrene standards). The data correspond to the polymer fraction of the isolated materials.

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Tables (cont.)

Table 4. Rh (I) catalyzed polymerization of calix[4]arene **2** with ternary catalytic system II[a,b]

Entry	[**2**]:[Rh]	Time (h)	Conversion (%)[b]	Reaction mixture composition (%)[b]			Isolated materials [b]		
				Polymer	Oligomers	Dimer	Yield (%)[c]	**Poly 2** (%)[b]	M_nx10^{-4} (M_w/M_n)[d]
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[e]	4.3 (1.67)
4	150	0.66	87.3	86.6	-	0.7	65.5	85.5[f]	4.4 (1.52)
5	50 [g]	1	97.6	97.3	-	0.3	82.5	97.9	1.7 (1.19)

[a] Typical conditions: [**2**]=0.1M, $[Rh(nbd)Cl]_2/Ph_2C{=}CPhLi/PPh_3$, $[PPh_3]$:[Rh]=5, toluene, 30ºC.[b] The degree of conversion, the composition of the polymerization mixture and that of isolated materials were evaluated by GPC.[c] Gravimetrically determined yield.[d] The M_n and polydispersity (M_w/M_n) were determined by GPC (THF, 35ºC, polystyrene standards). The data correspond to the polymer fraction of the isolated materials.[e] Additionally, a polymer (5.8%) with M_n=1.0x10^5 (M_w/M_n=1.18) was present.[f] A polymer (9.9%) with M_n=8.9x10^4 (M_w/M_n=1.18) was also present.[g] [**2**]=0.05M.

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Chart caption

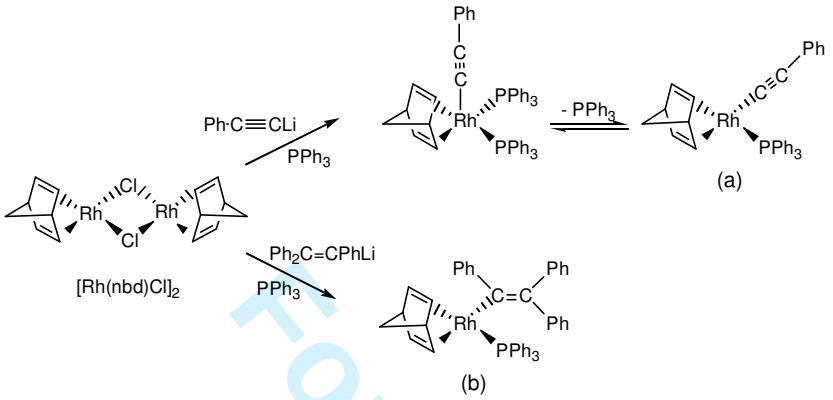

Chart 1. Catalytic systems introduced by (a) Noyori *et al.*[20] and (b) Masuda *et al.*[22] for the living polymerizations of arylacetylenes.

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Figure caption

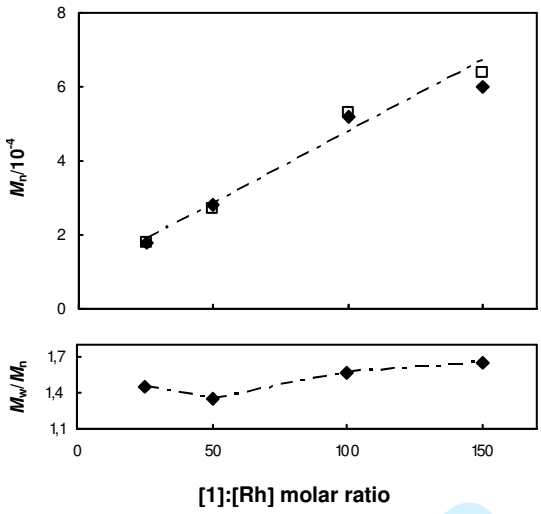

Figure 1. M_n and M_w/M_n of **poly 1** *vs* [**1**]:[Rh] molar ratios plots in the polymerization of calix[4]arene **1** by the TCS II; a) □, crude reaction mixture; b) ◆, isolated **poly 1**.

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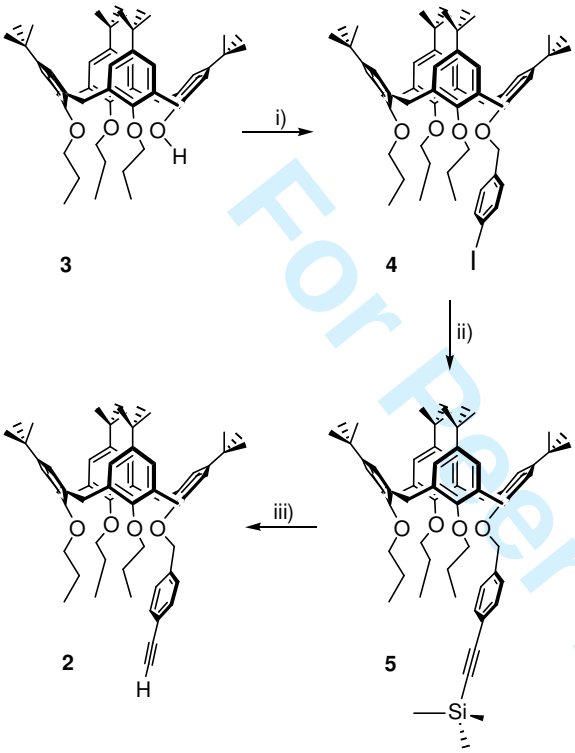
Scheme titles



Scheme 1. Synthesis of 25-(4-ethynylbenzyloxy)-26,27,28-tripropyloxycalix[4]arene **2**: i) $BrCH_2PhI$ (2.3 eq.), NaH (4.1 eq.), THF, reflux, 24h; ii) $Pd(OAc)_2$ (2.5 mol%), CuI (5 mol%), $(CH_3)_3SiC{\equiv}CH$ (1.2 eq.), PPh_3 (5 mol%), NEt_3, 50ºC, 24h; iii) K_2CO_3 (0.1 eq.), THF/MeOH, 25ºC, 22h.

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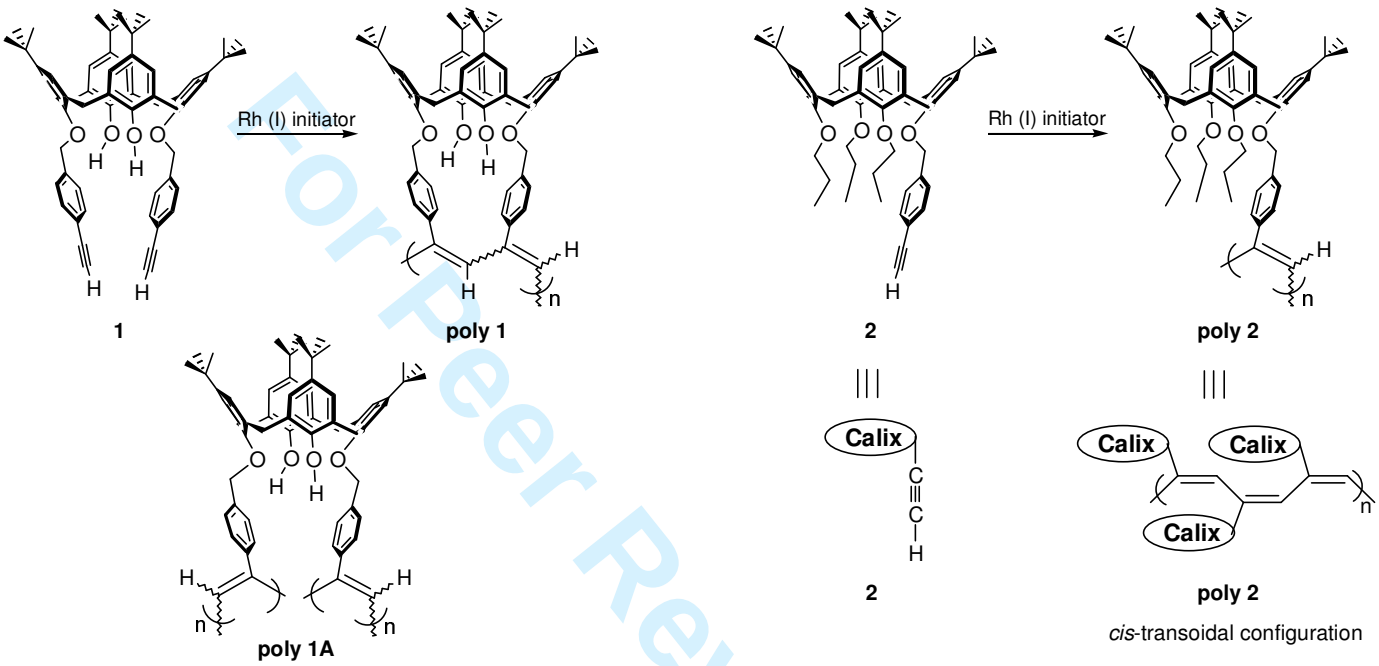
Scheme titles (cont.)



Scheme 2. Rh(I) catalyzed polymerization of calix[4]arenes **1** and **2** and the possible structures of the resulting polymers.[32]

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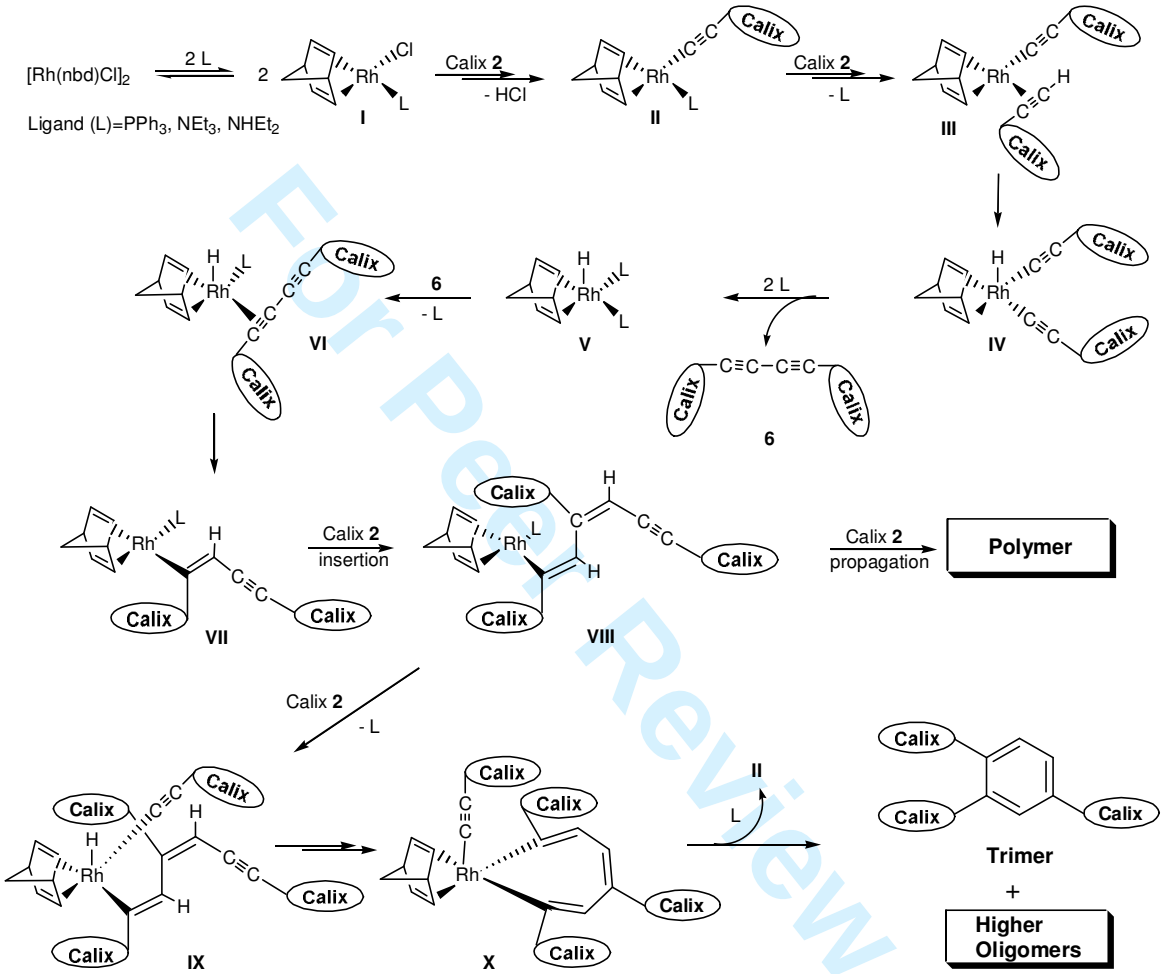
Scheme titles (cont.)



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.

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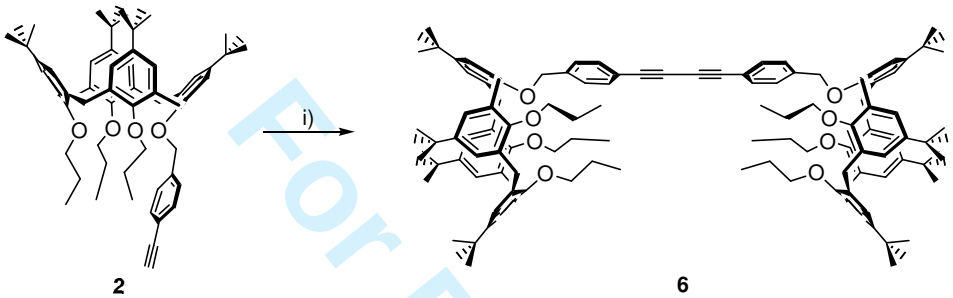
Scheme titles (cont.)



Scheme 4. Synthesis of dimer **6**: i) CuCl (5 mol%), TMEDA (5.7 mol%), toluene, 65ºC, 1.5h.

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Tables

Table 1. Rh (I) catalyzed polymerization of calix[4]arene **2** with binary catalytic systems[a,b]

Entry	Solvent	[**2**]	[**2**]:[Rh]	Co-catalyst (equiv/[Rh])	Time (h)	Conversion (%)[b]	Reaction mixture composition (%)[b]			M_nx10^{-4} (M_w/M_n)[c]
							Polymer	Oligomers	Dimer	
1	THF	0.2	25	PPh_3 (2)	4.5[d]	40.7	31.5	3.8	5.4	7.1 (2.31)
2	THF	0.05	50	$NHEt_2$ (100)	18.5[d]	48.3	1.6	41.9	4.8	6.0 (1.32)
3	THF	0.05	50	NEt_3 (100)	20[d]	66.7	2.9	57.7	6.2	- [e]
4	$CHCl_3$	0.07	25	$NHEt_2$ (25)	23	90.9	60.9	27.8	2.2	- [e]
5	$CHCl_3$	0.1	50	$NHEt_2$ (50)	6[d]	40.8	14.8	22.4	3.6	- [e]
6	$CHCl_3$	0.05	50	$NHEt_2$ (50)	24	94.1	19.2	69.6	5.7	- [e]
7	THF	0.1	50	*n*-BuLi (2.5)[f]	1	19.4	14.1	2.5	2.8	4.6 (2.51)

[a] Typical conditions: Monomer **2**, $[Rh(nbd)Cl]_2$, solvent and co-catalyst, 30ºC.[b] The degree of conversion and the composition of the polymerization mixture were evaluated by GPC.[c] The M_n and polydispersity (M_w/M_n) were determined by GPC (THF, 35ºC, polystyrene standards), and are referred to polymeric materials.[d] The reaction was quenched at this time due to its high viscosity, which had preventing adequate stirring of the contents.[e] Bimodal/multimodal distribution.[f] PPh_3 was also added ([phosphine]:[Rh]=5).

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Tables (cont.)

Table 2. Rh (I) catalyzed polymerization of calix[4]arenes **1** and **2** with ternary catalytic system I[a,b]

Entry	Monomer	[PhC≡CLi]:[Rh]	Additive (equiv/[Rh])	Time (h)	Conversion (%)[b]	Reaction mixture composition (%)[b]			M_nx10^{-4} (M_w/M_n)[c,d]
						Polymer	Oligomers	Dimer	
1	2	3.1[e]	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[e,f]	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 [e,f]	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 [e,f]	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[e,g]	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[e,g]	NEt_3 (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 [e]	NEt_3 (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_3 (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_3 (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_3 (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	-[h]	NEt_3 (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 [e]	NEt_3 (25)	1	76.8	75.0	-	1.8	8.6 (1.82)

[a] Typical conditions: [**2**]=0.1M, $[Rh(nbd)Cl]_2$/PhC≡CLi/PPh_3, [**2**]:[Rh]=50, [PPh_3]:[Rh]=5, toluene, 30ºC.[b] The degree of conversion and the composition of the polymerization mixture were evaluated by GPC.[c] Data refers to polymeric materials.[d] The M_n and polydispersity (M_w/M_n) were determined by GPC (THF, 35ºC, polystyrene standards).[e] Phenylacetylene was also present in the proportion: [PhC≡CH]:[PhC≡CLi]=0.6. [f] No aging period. [g] The catalytic system was aged at 30ºC for 2h.[h] A molar ratio of [PhC≡CH]:[Rh]=5 was used.

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Tables (cont.)

Table 3. Rh (I) catalyzed polymerization of calix[4]arene **1** with ternary catalytic system II[a,b]

Entry	[**1**]:[Rh]	Time (h)	Conversion (%)[b]	Reaction mixture composition (%)[b]			Isolated materials[b]		
				Polymer	Oligomers	Dimer	Yield (%)[c]	**Poly 1** (%)[b]	M_nx10^{-4} (M_w/M_n)[d]
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)

[a] Typical conditions: [**1**]=0.1M, $[Rh(nbd)Cl]_2/Ph_2C{=}CPhLi/PPh_3$, $[PPh_3]$:[Rh]=5, toluene, 30ºC.[b] The degree of conversion, the composition of the polymerization mixture and that of isolated materials were evaluated by GPC.[c] Gravimetrically determined yield.[d] The M_n and polydispersity (M_w/M_n) were determined by GPC (THF, 35ºC, polystyrene standards). The data correspond to the polymer fraction of the isolated materials.

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Tables (cont.)

Table 4. Rh (I) catalyzed polymerization of calix[4]arene **2** with ternary catalytic system II[a,b]

Entry	[**2**]:[Rh]	Time (h)	Conversion (%)[b]	Reaction mixture composition (%)[b]			Isolated materials[b]		
				Polymer	Oligomers	Dimer	Yield (%)[c]	**Poly 2** (%)[b]	M_nx10^{-4} (M_w/M_n)[d]
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[e]	4.3 (1.67)
4	150	0.66	87.3	86.6	-	0.7	65.5	85.5[f]	4.4 (1.52)
5	50[g]	1	97.6	97.3	-	0.3	82.5	97.9	1.7 (1.19)

[a] Typical conditions: [**2**]=0.1M, $[Rh(nbd)Cl]_2/Ph_2C{=}CPhLi/PPh_3$, $[PPh_3]$:[Rh]=5, toluene, 30ºC.[b] The degree of conversion, the composition of the polymerization mixture and that of isolated materials were evaluated by GPC.[c] Gravimetrically determined yield.[d] The M_n and polydispersity (M_w/M_n) were determined by GPC (THF, 35ºC, polystyrene standards). The data correspond to the polymer fraction of the isolated materials.[e] Additionally, a polymer (5.8%) with M_n=1.0x10^5 (M_w/M_n=1.18) was present.[f] A polymer (9.9%) with M_n=8.9x10^4 (M_w/M_n=1.18) was also present.[g] [**2**]=0.05M.

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