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New Stars: Eight Polyisobutylene Arms Emanating from a Calixarene Core[†]

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ABSTRACT: The first synthesis of well-defined star polymers consisting of eight polyisobutylene (PIB) arms emanating from a calixarene core is described. The synthesis was accomplished with the use of octafunctional calixarene derivative initiators which, in conjunction with $BCl_3/TiCl_4$ coinitiators, induce the living polymerization of isobutylene (IB). Specifically, the initiators were *tert*-hydroxy and *tert*-methoxy derivatives (**5** and **6**, respectively) of 5,11,17,23,29,35,41,47-octaacetyl-49,50,51,52,53,54,55,56-octamethoxycalix[8]arene. The *tert*-methoxy derivative (**6**) is soluble in polymerization charges (CH_3Cl/hexanes) at −80 °C and was used preferentially. To gain insight into the mechanism of polymerization, model experiments using a monofunctional analogue, 2-(*p*-methoxyphenyl)-2-methoxypropane (**8**), of the octafunctional initiators were also conducted. According to these model studies, **8** is an efficient initiator for the living polymerization of IB, and the initiator residue can be spectroscopically quantitated as the head group of PIB. Well-defined stars with close to theoretical composition and molecular weights were obtained in the presence of BCl_3-TiCl_4 mixtures; however, polymerizations were unsatisfactory with the use of only BCl_3 or only $TiCl_4$. Polymerizations were carried out in two stages in one reactor. In the first stage, the reaction was initiated with the **6**/BCl_3 combination using ~25% of the required amount of IB in CH_3Cl at −80 °C, followed by the second stage, in which hexanes, $TiCl_4$, and the balance of the monomer were added. Gel permeation chromatography, by the use of on-line RI, UV, and laser light scattering detectors, was used to determine the molecular weight and composition of the linear and octa-arm star polymers. The number-average number of arms, $\bar{N}_{n,arm}$, and the weight-average number of arms, $\bar{N}_{w,arm}$, were determined directly by core destruction of the calixarene moiety, followed by molecular weight determination of the surviving arms; according to these studies, $\bar{N}_{n,arm}$ and $\bar{N}_{w,arm}$ were 7.6 and 7.7, respectively.

I. Introduction

The synthesis of well-defined star polymers with a known number of arms, arm molecular weight, and narrow polydispersity is a challenge to the macromolecular engineer. To date, three major synthesis techniques have been described/used for the synthesis of stars: (a) use of multifunctional linking agents, (b) sequential copolymerization/linking with a divinyl monomer, and (c) use of multifunctional initiators.

The use of multifunctional linking agents has been proven effective by anionic techniques for the preparation of homo-,[1] block-,[2] and hetero-arm[3] star polymers with varying number of arms. Multifunctional carbocationic linking was used by Sawamoto and co-workers[4] in preparing well-defined tetra-arm poly(isobutyl vinyl ether) stars. Kennedy and co-workers prepared multi-arm polyisobutylene (PIB) stars by hydrosilylation of allyl-terminated PIB with cyclic hydromethylsiloxane cores.[5] Linking living polymer chains with a divinyl monomer has been used for the synthesis of multi-arm stars by anionic,[6] cationic,[7,8] and group transfer polymerization.[9] With the use of multifunctional initiators, the functional groups at the end of arms may be preserved during star formation. This method is limited, however, with anionic systems due to poor initiator solubility in hydrocarbons.[10,11] Eschwey and Burchard[12] and Lutz and Rempp[13] have independently shown that hydrocarbon-swollen polydivinylbenzene anions can be used as multifunctional initiators;[12,13] however, the dispersity of the stars was rather broad. Quirk and Tsai have recently used a hydrocarbon-soluble trifunctional initiator for the preparation of homo-, block-, and functionalized stars.[14] Solubility problems of multifunctional initiators are less of an issue in cationic polymerizations, and tri- and tetrafunctional initiators have been used to prepare well-defined three- and four-arm star polymers.[15−17] Except for two reports on the synthesis of hexa-arm polystyrene[18] and hexa-arm polyoxazoline,[19] there is a dearth of information in the literature in regard to well-defined multifunctional initiators for the preparation of higher functionality stars. This paper concerns the synthesis of octa-arm PIB stars by octafunctional initiators derived from calix[8]arenes.

Calix[*n*]arenes ($n = 4, 6, 8$) are cyclic condensation products of a para-substituted phenol and formaldehyde.[20] Gutsche and co-workers have developed various procedures for the selective synthesis of various calixarenes and calixarene derivatives.[21,22] Here we demonstrate that calixarene derivatives can be used as multifunctional initiators for the synthesis of well-defined PIB stars.

II. Experimental Section

A. Materials. *p-tert*-Butylphenol, paraformaldehyde, potassium hydroxide, xylene, $AlCl_3$, toluene, phenol, methyl iodide (99.9%), THF, NaH, acetyl chloride, $TiCl_4$, CCl_4, dimethylacetamide (DMA), di-*tert*-butylpyridine (DtBP), trifluoroacetic acid, $CDCl_3$, and pyridine-d_5 were from Aldrich and were used as received. Isobutylene (IB, CP grade) and methyl chloride (CH_3Cl) were obtained from Matheson and dried by passing them through in-line gas purifier columns packed with BaO/Drierite/molecular sieves/$CaCl_2$. Hexanes, CH_2Cl_2, HCl, diethyl ether, dimethyl formamide (DMF), and methanol were from Fischer Scientific. Hexanes and THF were refluxed overnight in the presence of CaH_2 and distilled before use. DMF was freshly distilled before use.

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B. Preparation of Octafunctional Initiators. (a) 5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,55,56-octahydroxycalix[8]arene (1). Following Gutsche's procedure,[21] a slurry of 111.2 g (0.72 mol) of *tert*-butylphenol, 36.0 g (1.2 mol) of paraformaldehyde, and 1.6 mL (0.016 mol) of 10 N KOH in 600 mL of xylene was refluxed under a N_2 atmosphere with stirring in a 1000 mL three-neck flask equipped with a Dean−Stark water collector. After refluxing for 20 min, the solid dissolved, and a white precipitate appeared after about 1 h. After refluxing for 4 h, the system was cooled and the solid filtered. The product was washed in sequence with 250 mL of toluene, ether, acetone, and water, dried under vacuum, and recrystallized from chloroform. Yield: 59% of **1**, a white powder. Gel permeation chromatography (GPC) showed a single peak. ^{1}H NMR: lit. (pyridine-d_5) δ 9.6 (s, 1, Ar-OH), 7.14 (s, 2, Ar-H), 4.3 (br d, 1, -CH_2-), 3.4 (br d, 1, -CH_2-), 1.24 (s, 9, $C(CH_3)_3$); obsd (pyridine-d_5) δ 9.6 (s, 1, Ar-OH), 7.1 (s, 2, Ar-H), 4.4 (br d, 1, -CH_2-), 3.5 (br d, 1, -CH_2-), 1.23 (s, 9, $C(CH_3)_3$).

(b) 49,50,51,52,53,54,55,56-Octahydroxycalix[8]arene (2). A slurry of 40 g (30.8 mmol) of **1**, 23.2 g (248 mmol) of phenol, 49.4 g (372 mmol) of $AlCl_3$, and 600 mL of toluene was stirred in a 1000 mL three-neck flask for 2 h at room temperature under nitrogen atmosphere. The mixture was added to 200 mL of cold water. The product dispersed as a white gelatinous precipitate in the organic layer, which was thoroughly washed with water. The toluene was removed by rotary evaporation, and the solid was washed in succession with acetone-HCl, methanol, $CHCl_3$, acetone, and diethyl ether to afford 25.0 g of a light gray solid. Yield: 95% of **2**. The product was insoluble in common organic solvents. ^{1}H NMR: lit. (pyridine-d_5) δ 6.0−7.0 (m, 3, Ar-H), 3.5 (br s, 2, -CH_2-); obsd (pyridine-d_5) δ 6.0−7.0 (m, 3, Ar-H), 3.4 (br s, 2, -CH_2-).

(c) 49,50,51,52,53,54,55,56-Octamethoxycalix[8]arene (3). In a 2000 mL three-neck flask equipped with stirrer and condenser, 26.8 g (31.6 mmol) of **2** was suspended in 1200 mL of THF and 120 mL of freshly distilled DMF under nitrogen. NaH (26.8 g, 1.13 mol) was added with stirring. When the bubbling has ceased, 254 g (1.73 mol) of CH_3I was added dropwise into the charge. After refluxing for 18 h, the system was cooled, and the solvents were removed by rotary evaporation. The solid was washed with plenty of water, five times with 100 mL portions of methanol, and finally with hexane to afford 27.2 g of a yellowish white powder, which was found to be essentially pure by ^{1}H NMR spectroscopy. Yield: 89% of **3**. ^{1}H NMR: lit. ($CDCl_3$) δ 6.8 (s, 3, Ar-H), 4.0 (s, 2, -CH_2-), 3.5 (s, 3, OCH_3); obsd ($CDCl_3$) δ 6.9 (br s, 3, Ar-H), 4.0 (s, 2, -CH_2-), 3.5 (s, 3, OCH_3).

(d) 5,11,17,23,29,35,41,47-Octaacetyl-49,50,51,52,53,54,55,56-octamethoxycalix[8]arene (4). In a 250 mL three-neck flask equipped with stirrer and condenser, 10 g (10.4 mmol) of **3** was dissolved in 90 mL of CH_2Cl_2 at 0 °C. A slurry of 13.92 g (104.8 mmol) of $AlCl_3$ in 35.7 mL (502.2 mmol) of acetyl chloride was added slowly with stirring. After being stirred for 2 h, the mixture was allowed to warm to room temperature and was stirred for another 2 h. The reaction was quenched by 400 mL of water, the organic layer was separated, the volatiles were evaporated, the solid was washed five times with 100 mL portions of methanol, dried under vacuum, and recrystallized from $CHCl_3$/methanol (75:25). Yield: 84% of **4**. ^{1}H NMR: lit. ($CDCl_3$) δ 7.6 (s, 2, Ar-H), 4.1 (s, 2, -CH_2-), 3.6 (s, 3, OCH_3), 2.4 (s, 3, -$C(O)CH_3$); obsd ($CDCl_3$) δ = 7.5 (s, 3, Ar-H), 4.0 (s, 2, -CH_2-), 3.6 (s, 3, OCH_3), 2.3 (s, 3, $C(O)CH_3$).

(e) 5,11,17,23,29,35,41,47-Octakis(2-hydroxypropyl)-49,50,51,52,53,54,55,56-octamethoxycalix[8]arene (5). Into a 2000 mL three-neck flask equipped with stirrer, condenser, and an addition funnel, under N_2, was added 339 g (1.01 mmol) of methylmagnesium bromide dropwise. In a separate round-bottom flask, 9.1 g (6.96 mmol, or 55.7 mmol equiv of C(O)-CH_3 groups) of **4** was dissolved in 900 mL of hot (∼70 °C) anisole, cooled, and added dropwise to the Grignard solution over a period of 1 h at 40 °C. After being stirred at room temperature for 30 h, the charge was added to ice-cold water. Aqueous NH_4Cl (50%) was added to dissolve most of the gelatinous precipitate. The aqueous layer was extracted five times with 50 mL portions of anisole and a small amount of ether, the organic layer was dried over $MgSO_4$ and filtered, and the product was precipitated using excess hexane. The solid was filtered, washed with hexane to remove traces of anisole, and dried in vacuum to give **5**. Yield: 72%. According to NMR (see Figures 4 and 5) analyses, the product was essentially pure. This compound appears to be novel. ^{1}H NMR: ($CDCl_3$) δ 6.9 (s, 2, Ar-H), 4.0 (s, 2, -CH_2-), 3.5 (s, 3, OCH_3), 2.8 (br s, 1, *tert*-OH), 1.22 (s, 6, $>C(CH_3)_2$). ^{13}C NMR: δ 61.0 (CH_3 of Ar-OCH_3), 155.6 (aromatic C attached to OCH_3), 133.8 (aromatic C attached to -CH_2- bridge), 30.5 (C of -CH_2- bridge), 125.8 (aromatic C attached to H), 145.3 (aromatic C attached to isopropyl group), 72.1 (*tert*-C attached to OH group), 31.5 (CH_3 of isopropyl group). Elemental analysis: (MW calcd for $C_{88}H_{112}O_{16}$, 1433 g/mol). Calcd: C, 74.15; H, 7.86. Obsd: C, 73.73; H, 8.36. mp (DSC) = 174 °C.

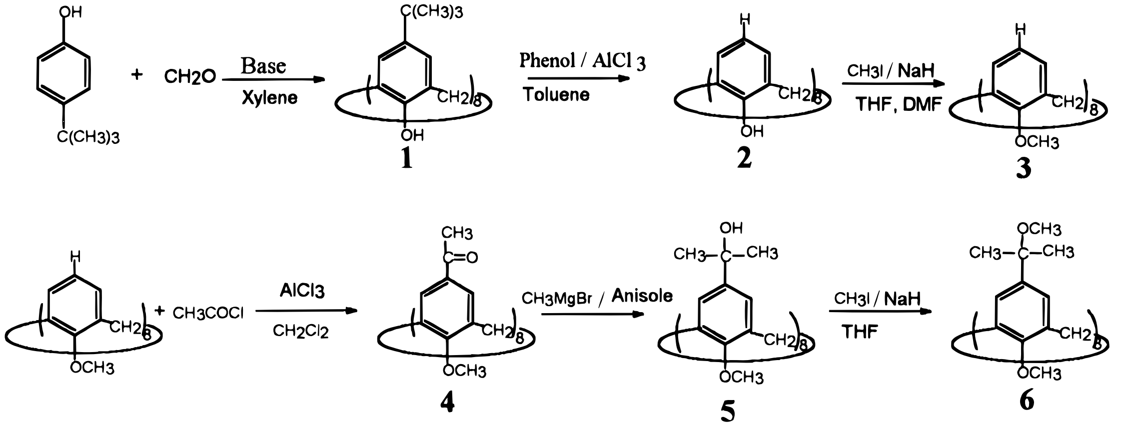
(f) 5,11,17,23,29,35,41,47-(2-Methoxypropyl)-49,50,51,52,53,54,55,56-octamethoxycalix[8]arene (6). In a 250 mL three-neck flask equipped with stirrer and condenser, 4 g (2.79 mmol) of **5** was dissolved in 150 mL of THF. Sodium hydride (1.62 g, 67.5 mmol), was added with caution. When the bubbling ceased, 32.0 g (225.7 mmol) of CH_3I was added dropwise to the charge. After being stirred for 16 h at room temperature, the reaction was quenched by addition of 50 mL of cold water. The organic layer was extracted five times with 50 mL portions of ether, the ether extract was dried over $MgSO_4$, and the solvent was evaporated to yield a pale yellow solid, which was triturated with hexanes and washed with hexanes to afford pure **6**. Yield: 75%. This compound appears to be novel. ^{1}H NMR (Figure 6): ($CDCl_3$) δ 6.9 (s, 2, Ar-H), 4.0 (s, 2, -CH_2-), 3.4 (s, 3, OCH_3), 2.9 (s, 3, *tert*-OCH_3), 1.3 (s, 6, $>C(CH_3)_2$). ^{13}CNMR (Figure 7): δ 60.8 (CH_3 of Ar-OCH_3), 156.0 (aromatic C attached to OCH_3), 134.0 (aromatic C attached to -CH_2- bridge), 30.5 (C of -CH_2- bridge), 127.0 (aromatic C attached to H), 141.2 (aromatic C attached to isopropyl group), 76.7 (*tert*-C attached to OCH_3 group), 28.0 (CH_3 of isopropyl group), 50.6 (C in CH_3O of -$C(CH_3)_2OCH_3$). Elemental analysis: (MW calcd for $C_{96}H_{128}O_{16}$, 1536 g/mol). Calcd: C, 75.13; H, 8.36. Obsd: C, 75.14; H, 8.64. mp(DSC) = 240 °C.

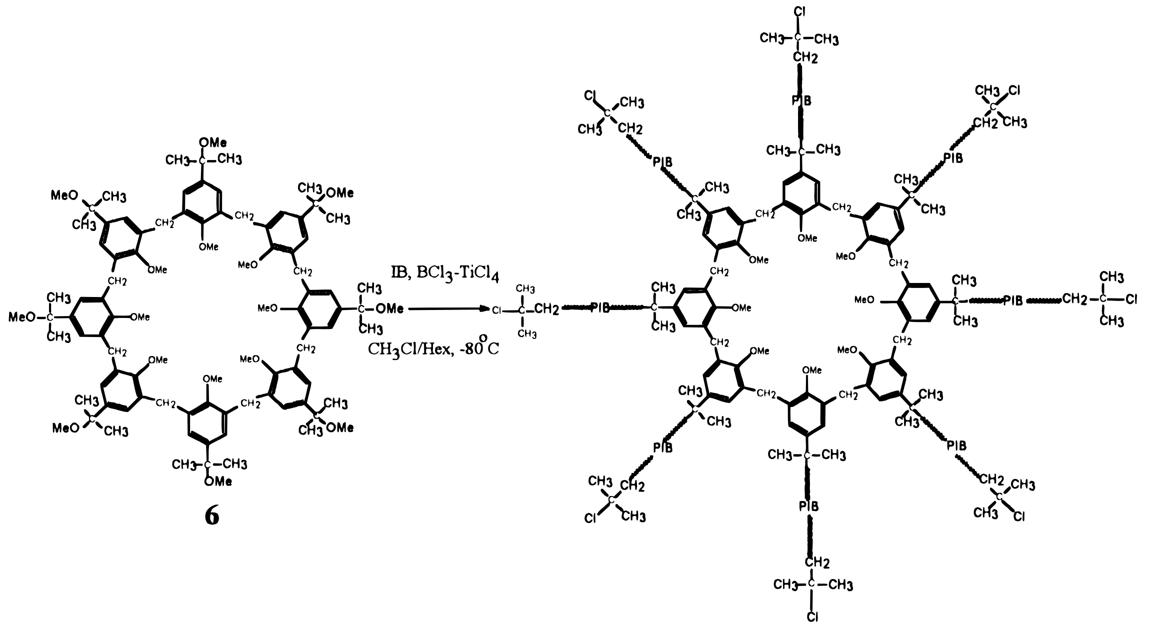
C. Preparation of Monofunctional Initiators. (a) 2-(*p*-Methoxyphenyl)-2-propanol (7). A 500 mL three-neck flask equipped with a mechanical stirrer, addition funnel, and water condenser was purged with N_2. Methylmagnesium bromide (3 M; 143 g, 138 mL, 0.41 mol) was added dropwise, followed by 50 mL of distilled THF. *p*-Methoxyacetophenone (31.1 g, 0.21 mol), dissolved in 100 mL of THF, was added dropwise to the Grignard reagent over a period of 1 h. After 12 h of stirring at room temperature, the mixture was slowly added to ice-cold water. Aqueous NH_4Cl (50%) was added to dissolve most of the gelatinous precipitate, the aqueous layer was extracted five times with 50 mL portions of diethyl ether, the ether extract dried over $MgSO_4$, and the solvent was evaporated under vacuum. Yield: 91% of clear, colorless liquid **7**. ^{1}H NMR ($CDCl_3$): δ 7.4 , 7.3 (d, 2 aromatic H ortho to OCH_3), 6.9, 6.8 (d, 2, aromatic H ortho to isopropyl group), 3.8 (s, 3, OCH_3), 1.8 (s, 1, OH), 1.5 (s, 6, $>C(CH_3)_2$).

(b) 2-(*p*-Methoxyphenyl)-2-methoxypropane (8). In a 500 mL three-neck flask equipped with a mechanical stirrer and condenser under nitrogen was added 31.2 g (0.19 mol) of **7** dissolved in 200 mL of THF. Sodium hydride (13.5 g, 0.56 mol) was added with caution. When the bubbling ceased, 160 g (1.08 mol) of CH_3I was added dropwise to the charge. After being stirred at room temperature for 16 h, the reaction was quenched by cold water, the organic layer was extracted three times with 50 mL portions of ether, the ether extract was dried over $MgSO_4$, and the solvent was evaporated under vacuum. Yield: 95% of crude product **8**. Vacuum distillation at 15 mmHg at 145 °C yielded essentially pure **8** by ^{1}H NMR spectroscopy. ^{1}H NMR ($CDCl_3$, Figure 1): δ 7.3 (d, 2, aromatic H ortho to OCH_3), 6.8 (d, 2, aromatic H ortho to isopropyl group), 3.8 (s, 3, Ar-OCH3), 3.0 (s, 3, *tert*-OCH_3), 1.5 (s, 6, $>C(CH_3)_2$).

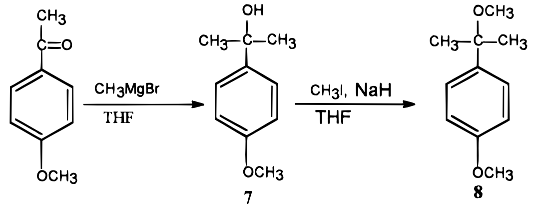
D. Polymerizations. (a) Polymerization of Isobutylene by the 2-(*p*-Methoxyphenyl)-2-methoxypropane (8)/BCl_3−$TiCl_4$ Initiating System. Polymerizations were car-

Scheme 1. "Core-First" Synthetic Strategy





Scheme 2. Synthesis of Monofunctional Initiators



ried out in 75 mL culture tubes in a stainless steel glovebox under dry nitrogen at −80 °C. The total volume of the charges was 29 mL. Polymerizations were carried out in two stages according to a published procedure.[26] In the first stage, the addition sequence of the reactants was CH_3Cl (7−8 mL), IB (∼25% of the required amount), initiator **8**, DMA, DtBP, and BCl_3. Stock solutions of initiator, DMA, DtBP, and BCl_3 were prepared in CH_3Cl. Care was taken not to freeze the $TiCl_4$ stock solution. After polymerizing for 30−60 min, hexanes, $TiCl_4$, and the balance of the monomer were added. Additions were made such that the CH_3Cl/hexanes ratio should remain 40:60 and the final volume would be 29 mL. By using the all-monomer-in (AMI) technique,[23] parallel runs were terminated using prechilled methanol at different times. The incremental monomer addition (IMA) technique[23] was also carried out for diagonostic purposes. The solvents were evaporated, the polymer was redissolved in hexanes, the hexanes layer was washed with 5% HCl, water, and methanol, and the polymer was dried in vacuo at room temperature. These polymers carry a 4-methoxyphenyl head-group and a *tert*-Cl tail-group (see Figure 3).

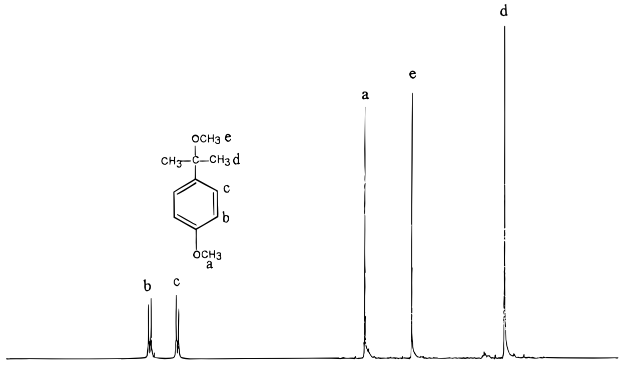


Figure 1. ^1H NMR ($CDCl_3$) spectrum of 2-(*p*-methoxyphenyl)-2-methoxypropane (**8**).

(b) Polymerization of Isobutylene by the 2-(*p*-Methoxyphenyl)-2-methoxypropane (8)/BCl_3 Initiating System. As described above, polymerizations were carried out in 75 mL culture tubes in a drybox at −80 °C. Initiator **8** (0.17 g, 3.84×10^{-2} M) was dissolved in 25 mL of CH_3Cl, and then, in sequence, IB (4 mL), DMA (6.62×10^{-2} M), and DtBP (3.41×10^{-2} M) were added, and the polymerization was induced by the addition of 1.14 mL (0.53 M) of BCl_3. After 3 h, the polymerization was quenched with prechilled methanol, and the polymer was purified as described above. ^1H NMR spectra were recorded by the use of $CDCl_3$ (see Figure 3 for peak assignments). The oligomers had a 4-methoxyphenyl head-group and a *tert*-Cl tail-group.

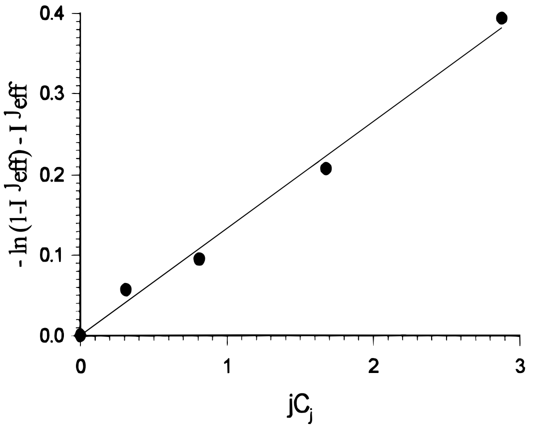


Figure 2. Plot of $-\ln(1 - I_{\mathrm{eff}}{}^{j}) - I_{\mathrm{eff}}{}^{j}$ versus jC_j of IB polymerization with 2-(*p*-methoxyphenyl)-2-methoxypropane (**8**) as initiator and BCl_3-TiCl_4 coinitiators.

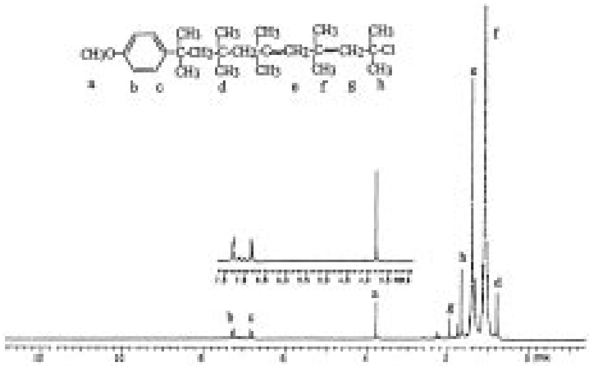
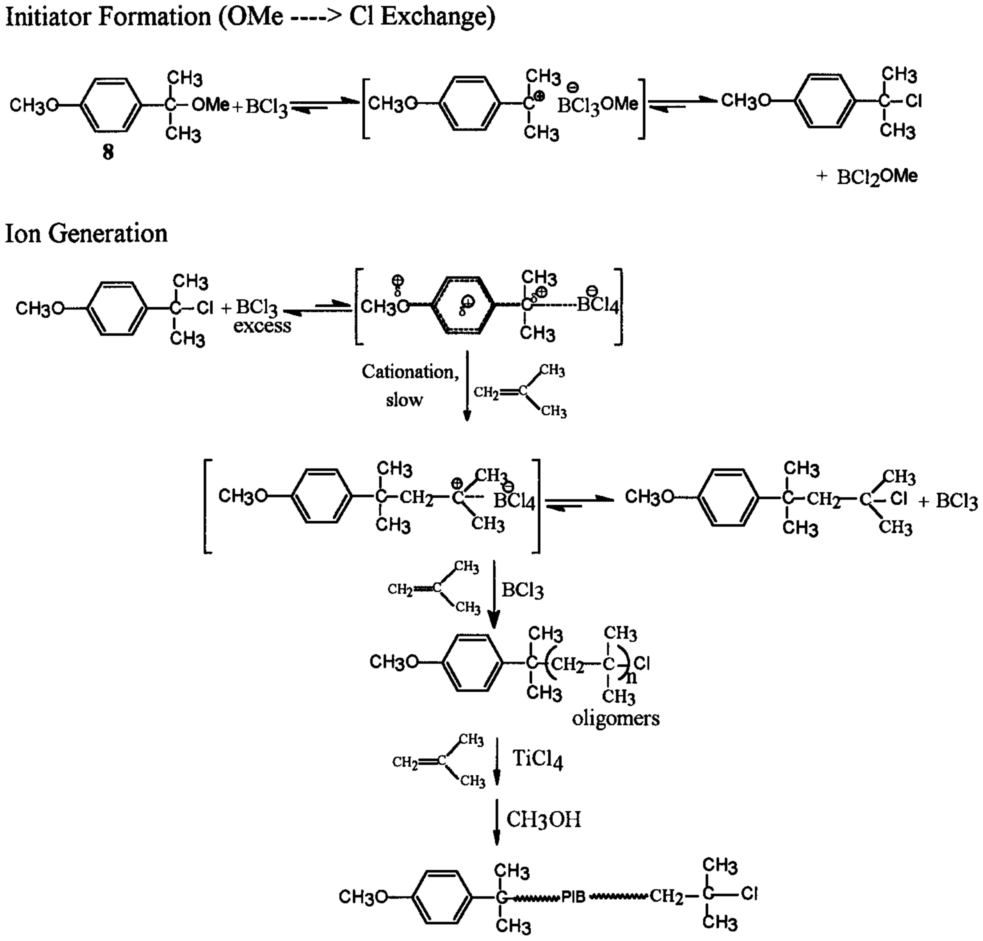


Figure 3. ^1H NMR ($CDCl_3$) spectrum of isobutylene oligomers ($\bar{M}_n$ = 1600 g/mol) prepared from 2-(*p*-methoxyphenyl)-2-methoxypropane (**8**) initiator and BCl_3 coinitiator.

(c) Polymerization of Isobutylene by the 5/BCl_3-TiCl_4 Initiating System. A procedure similar to the one described above was followed with some changes in the reactants charging sequence. Initiator **5** (0.0516 g, 1.24×10^{-3} M) was suspended in 8 mL of CH_3Cl, and then BCl_3 (0.68 mL, 0.32 M) was added, the was charge aged for 5 min, and then DMA (1.98×10^{-2} M) and DtBP (4.97×10^{-3} M) were added. After 10 min, 1.5 mL (38% of the required amount) of IB was added to start the polymerization. After 2 h, 14 mL of hexanes, $TiCl_4$ (4.97×10^{-2} M), and the remaining amount of IB (2.5 mL) were added. After 1 h, the polymerization was terminated with prechilled methanol and the product worked-up as described above. GPC analysis (see Figure 8) showed the presence of two major products: star polymer, ~70%, and a side product, ~30%. The star polymer was isolated from the mixture by fractionation using hexanes as the solvent and acetone as the precipitating agent.

(d) Polymerization of Isobutylene by the 6/BCl_3-TiCl_4 Initiating System. The two-stage procedure was carried out as described in section D(a), except with the use of initiator **6**. Polymerizations were carried out either in 75 mL culture tubes or in 250 mL stirred reactors. In the first stage, the addition sequence of the reactants was initiator, **6**, CH_3Cl, IB (~25% of the required amount), DMA, DtBP, and BCl_3. Stock solutions of initiator, DMA, DtBP, and BCl_3 were prepared in CH_3Cl. Care was taken not to freeze the $TiCl_4$ stock solution. After polymerizing for 60 min, hexanes, $TiCl_4$, and the balance of IB were added. The CH_3Cl/hexanes ratio (v/v) was always 40:60. Higher molecular weight stars were prepared by the IMA technique. Care was taken to keep the concentration of the charges constant by adding solvents and other ingredients. GPC analysis (see Figure 10) showed the presence of two major

Scheme 3. Slow Initiation Mechanism



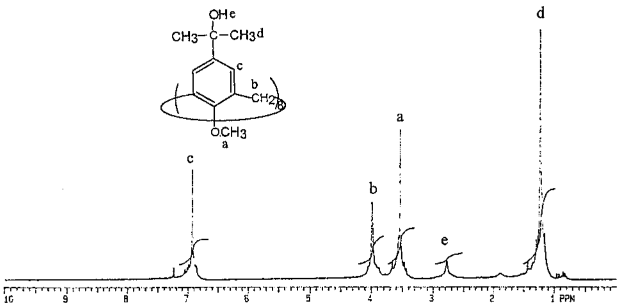


Figure 4. ^{1}H NMR (CDCl$_3$) spectrum of 5,11,17,23,29,35,41,47-octakis(2-hydroxypropyl)-49,50,51,52,53,54,55,56-octamethoxycalix[8]arene (**5**).

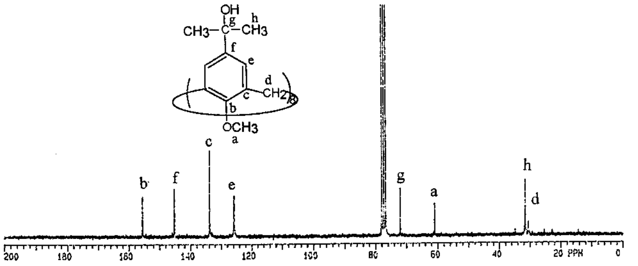


Figure 5. ^{13}C NMR (CDCl$_3$) spectrum of 5,11,17,23,29,35,41,47-octakis(2-hydroxypropyl)-49,50,51,52,53,55,56-octamethoxycalix[8]arene (**5**).

products: star polymer, ~90%, and a side product, ~10%. The star polymer was isolated from the mixture by fractionation using hexanes as the solvent and acetone as the precipitating agent.

Polymerization using only TiCl$_4$ was carried out in a single stage. The addition sequence of the reactants was initiator, CH$_3$Cl/hexanes, IB, DMA, DtBP, and TiCl$_4$. All polymerizations were carried out to near complete conversions.

E. Core Destruction of Star Polymers. Star polymer ($\bar{M}_w$(LLS) = 1.159 × 10^5 g/mol, entry 2, Table 3), 0.26 g, was dissolved in 25 mL of CCl$_4$ in a 250 mL two-neck round-bottom flask fitted with a condenser and N$_2$ inlet. A mixture of 14 mL of trifluoroacetic acid and 4 mL of 30% aqueous H$_2$O$_2$ was added with stirring. The charge was refluxed at 75–80 °C; samples were withdrawn in 2 h intervals, quenched by methanol, evaporated to dryness, redissolved in hexanes, precipitated using methanol, and dried in vacuum. GPC analysis of a sample withdrawn after 16 h indicated a single peak (i.e., complete core destruction) $\bar{M}_w$(LLS) = 1.496 × 10^4 g/mol).

Control experiments were carried out under identical conditions using a linear PIB ($\bar{M}_n$ ~10 000 g/mol, $\bar{M}_w/\bar{M}_n = 1.2$) and **1**. GPC analysis of the samples indicated that the calixarene was destroyed and formed low molecular weight products, whereas PIB survived the oxidation.

F. Characterization. ^{1}H NMR and ^{13}C NMR spectra (~30 and ~50 mg samples, respectively) were recorded on a Varian Gemini-200 spectrometer using standard 5 mm tubes at room temperature. For ^{1}H NMR spectroscopy, 64 FIDs were collected, and for ^{13}C NMR spectroscopy, more than 4000 FIDs were collected. Melting points of octafunctional initiators were determined with a Dupont differential scanning calorimeter in N$_2$ atmosphere. Elemental analyses were performed by Galbriath Laboratories Inc. (Knoxville, TN).

Molecular weights were determined by GPC (Waters Co.) equipped with a series of five Styragel microcolumns (100, 500, 10^3, 10^4, and 10^5), a RI detector (Waters 410 differential refractometer), a UV detector (440 absorbance detector), WISP 7103 with Nelson analytical interfaces, and a laser light scattering (LLS) detector (Wyatt Technology). The columns were calibrated using narrow molecular weight PIB standards. Approximately 20 mg of polymer and a few crystals of sulfur (internal standard) were dissolved in 4 mL of THF, the solution was filtered by using a 0.2 μm Acrodisc filter (membrane type PTFE), and 100 μL samples were injected by the auto injector.

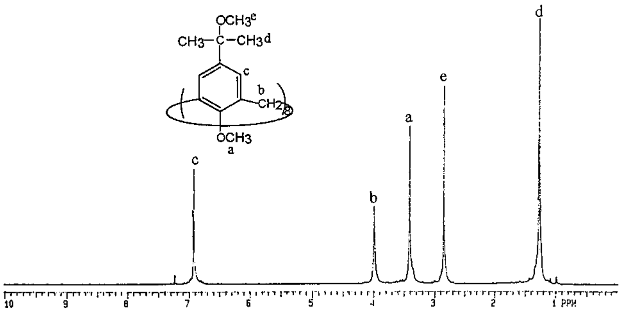


Figure 6. ^{1}H NMR (CDCl$_3$) spectrum of 5,11,17,23,29,35,41,47-octakis(2-methoxypropyl)-49,50,51,52,53,54,55,56-octamethoxycalix[8]arene (**6**).

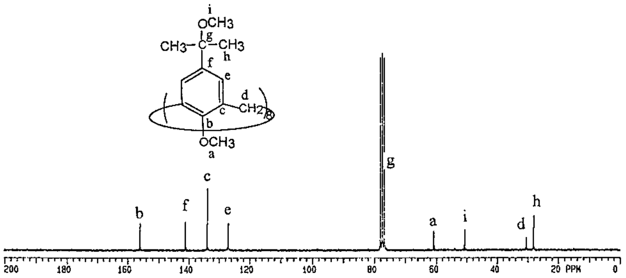


Figure 7. ^{13}C NMR (CDCl$_3$) spectrum of 5,11,17,23,29,35,41,47-octakis(2-methoxypropyl)-49,50,51,52,53,54,55,56-octamethoxycalix[8]arene (**6**). The peak corresponding to the *tert*-C attached to the OMe group, $\delta = 76.7$ ppm, is superimposed on the CDCl$_3$ peaks.

The Nelson Analytical Gel Permeation Chromatography software (version 4.0) was used for data analysis.

The d*n*/d*c* values were obtained by using an Optilab 903 (Wyatt Technology) instrument. Polymers were dissolved in THF prefiltered by 0.025 μm Whatman Anotop 25 filters, and the solutions were filtered using 0.2 μm Acrodisc filters (membrane type PTFE), evaporated to dryness in air under dust-free conditions, and further dried under vacuum. These samples were used for preparing polymer solutions of known concentrations (e.g., 1.5 × 10^{-4} g/μL) using prefiltered THF. Polymer solutions (100 μL) were injected into the columns using the autoinjector. Astra software (version 4.00, Wyatt Technology Corp.) was used for data analysis.

III. Results and Discussion

The objective of this research was the preparation of novel octa-arm star polymers consisting of eight PIB arms emanating from a calix[8]arene core. The preparative strategy called for the precision synthesis of calix[8]arene derivative **6** carrying eight initiating sites for the living polymerization of IB and its use to induce the living polymerization of IB to desirable arm lengths. Scheme 1 helps to visualize the structures involved and the key steps of this "core-first" method.

To gain insight into the polymerization mechanism, model experiments have been carried out with a monofunctional analogue (**8**) of the octafunctional initiator.

In this section, we will first discuss the results of model experiments and then present our synthesis research, which culminated in the preparation of the novel octafunctional stars, and we will conclude by detailing the characterization of a representative star comprising eight PIB arms, each capped by a *tert*-chlorine group, emanating from a calixarene core.

A. Model Experiments. To provide guidance for the synthesis of eight-arm stars by octafunctional calixarene initiator, model polymerizations have been performed using the monofunctional analogue, **8**. This novel initiator was prepared by a two-step procedure

Table 1. Elemental Analysis of Octafunctional Initiators 5 and 6

compound (formula)	element	% composition calcd	obsd
5, $C_{88}H_{112}O_{16}$	H	7.86	8.36
	C	74.15	73.73
6, $C_{96}H_{128}O_{16}$	H	8.36	8.64
	C	75.13	75.14

as outlined in Scheme 2. Figure 1 shows the ^1H NMR spectrum of **8**, together with peak assignments.

Model living IB polymerizations were effected by the use of initiator **8** under conditions employed for the synthesis of the eight-arm PIB star with initiator **6**. Thus, IB was polymerized in two stages with BCl_3-TiCl_4 coinitiators at −80 °C (see also section III.B(b)). Stage I was carried out in the presence of a fraction of the required amount of IB plus BCl_3 in CH_3Cl at −80 °C. During this stage only very low conversions and very low average molecular weights are obtained which indicate that only a few IB units are added to the initiator. Stage II was induced by the addition of $TiCl_4$, hexanes, and the balance of IB, and the polymerization was carried to completion.

Livingness was proven by the IMA technique and plotting the results according to the equation derived for living polymerization proceeding with slow initiation:[24]

$$-\ln(1 - I^{j}_{\text{eff}}) - I^{j}_{\text{eff}} = j\,\frac{k_c}{k_p}\,\frac{[\Delta M]}{[I_0]}C_j$$

where j is the number of monomer increments, k_c and k_p are the rate constants of cationation and propagation, respectively, $[\Delta M]$ is the total amount of monomer increment, $[I_0]$ is the initiator concentration, C_j is the apparent monomer conversion, and $I_{\text{eff}}{}^{j}$ is the initiator efficiency at j increments. Figure 2 shows a plot of $-\ln(1 - I_{\text{eff}}{}^{j}) - I_{\text{eff}}{}^{j}$ versus jC_j. The linearity of the plot starting from the origin indicates living polymerization with slow initiation.

Slow initiation is most likely due to the formation of a resonance-stabilized carbocation, which causes cationation to be rate limiting. Scheme 3 illustrates the species involved in this polymerization. Detailed kinetic investigations of IB polymerization by initiator **8** are described elsewhere.[25]

To prove that the primary ether group in the initiator moiety remains intact during polymerization and workup, IB oligomers were prepared to facilitate spectroscopic analysis. Figure 3 shows a representative ^1H NMR spectrum, together with assignments of this product. Integrated peak areas of aromatic protons (δ = 7.4−6.8 ppm), protons of methoxy group, Ar-OCH_3 (δ = 3.8 ppm), and protons of the terminal methylene groups in the chain (δ = 1.95 ppm) indicate quantitative initiator incorporation and the presence of Ar-OCH_3 in the polymer.

B. Synthesis and Characterization of the Novel Stars. Guided by the results of model experiments, IB polymerizations have been carried out using octafunctional initiators **5** and **6**. This section concerns the synthesis and characterization of **5** and **6**, subsequent polymerization experiments effected with these initiators, and experiments that prove the structure of the stars.

(a) Synthesis and Characterization of Octafunctional Initiators. Scheme 1 shows the route for the preparation of **5** and **6**. The first four steps have been described by Gutsche and co-workers.[21,22] Briefly, these steps involve the cyclic condensation of *p*-*tert*-butylphenol and paraformaldehyde in the presence of KOH to obtain **1**, dealkylation of *p*-*tert*-butyl groups by $AlCl_3$ in the presence of phenol to give **2**, and protection of the OH groups as the methyl ether **3**, which enables subsequent acylation to **4**. Product **4** was found to be sparingly soluble in diethyl ether and THF, and an attempt of a heterophase Grignard reaction in THF to prepare **5** was unsuccessful. In contrast, the solubility of **4** in anisole was sufficient (1 g in 100 mL) for the Grignard synthesis. Since **5** contains eight *tert*-OH groups, the danger of dehydration during solvent removal at higher temperatures and reduced pressures exists. Thus, **5** was recovered by precipitation by the addition of excess nonsolvent (hexanes) to the anisole extract. Product recovery from the filtrate was maximized by evaporating at room temperature. ^1H NMR (Figure 4) and ^{13}C NMR (Figure 5) spectroscopy indicated the presence of essentially pure **5**. Elemental analysis of **5** (see Table 1) showed a slightly higher H content (8.36%) than the calculated value (7.86%), which may be due to the tendency of the hydroxyl groups to bond water.

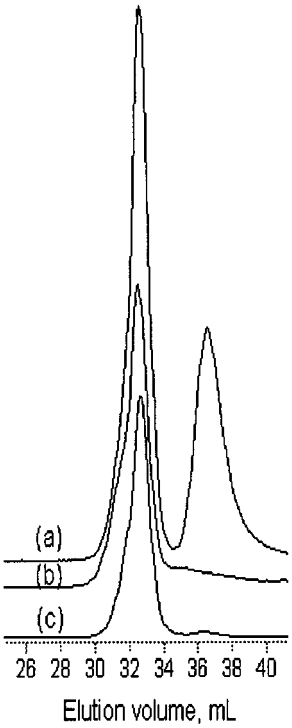


Figure 8. Gel permeation chromatograms: (a) RI trace and (b) UV trace of polymers before fractionation; (c) RI trace of stars after fractionation of star polymer obtained by using the **5**/BCl_3-TiCl_4 initiating system.

5 was converted to **6** by using CH_3I under basic conditions at room temperature in THF. The ^1H NMR (Figure 6) and ^{13}C NMR (Figure 7) spectra, together with elemental analysis, showed the presence of eight *tert*-ether groups in **6**.

(b) Polymerization of IB Using Octafunctional Initiators 5 and 6. Initial polymerization attempts were made with the octafunctional initiator **5**; however, this derivative was found to be insufficiently soluble in CH_3Cl at −80 °C for systematic investigations. Subsequently, in the hope that the *tert*-Cl derivative of **5**, which can be conveniently made *in situ* by contacting the *tert*-OH in **5** with BCl_3, would provide a soluble

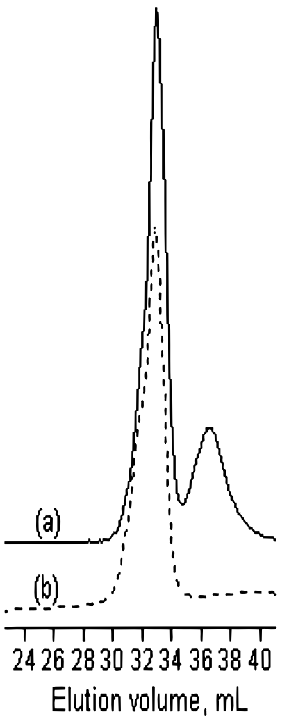
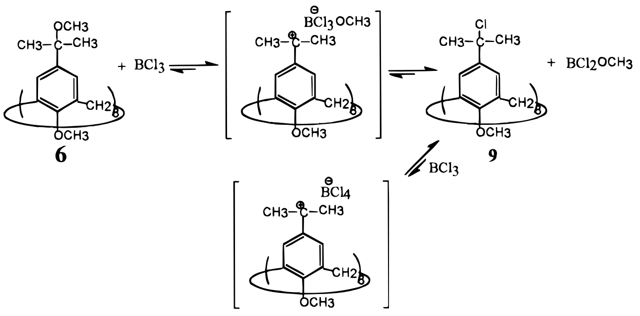


Figure 9. Gel permeation chromatograms: (a) RI trace and (b) UV trace of polymers obtained by using the **6**/BCl_3-TiCl_4 initiating system (for conditions, see expt 1, Table 2).

Scheme 4. Intermediates Involved in IB Polymerization Using 6



initiator, we have carried out a two-stage polymerization as follows: **5** was aged with BCl_3 in CH_3Cl at −80 °C, and then a fraction of the amount of IB was added (stage I), and finally $TiCl_4$ and the balance of the IB were added (stage II). Prior experience accumulated in these laboratories has shown that BCl_3-TiCl_4 mixtures[26,27] are better coinitiators in certain instances than either of these Friedel−Crafts halides alone. Gratifyingly, by using BCl_3 and $TiCl_4$ in two stages, we have obtained rapid polymerizations and complete conversions. Figure 8 shows the GPC (RI and UV) traces of the product. According to the RI scan, two products have formed: the large RI peak (and the corresponding UV peak) at relatively high molecular weights (~32 mL) is most likely due to the sought star formed by controlled initiation (UV absorption indicates the presence of calixarene core), while the smaller RI-active (UV-inactive) peak suggests a linear PIB byproduct. The latter most likely arose by side reaction(s) (see description hereinafter). Both the main (star) product and the linear byproduct exhibit narrow dispersities, $\bar{M}_w/\bar{M}_n$ = 1.14 and 1.2, respectively. The two products can be readily separated by reprecipitation from hexanes with acetone. Figure 8c shows the RI trace of the star after fractionation.

Scheme 5. Competing Reactions during Star Formation

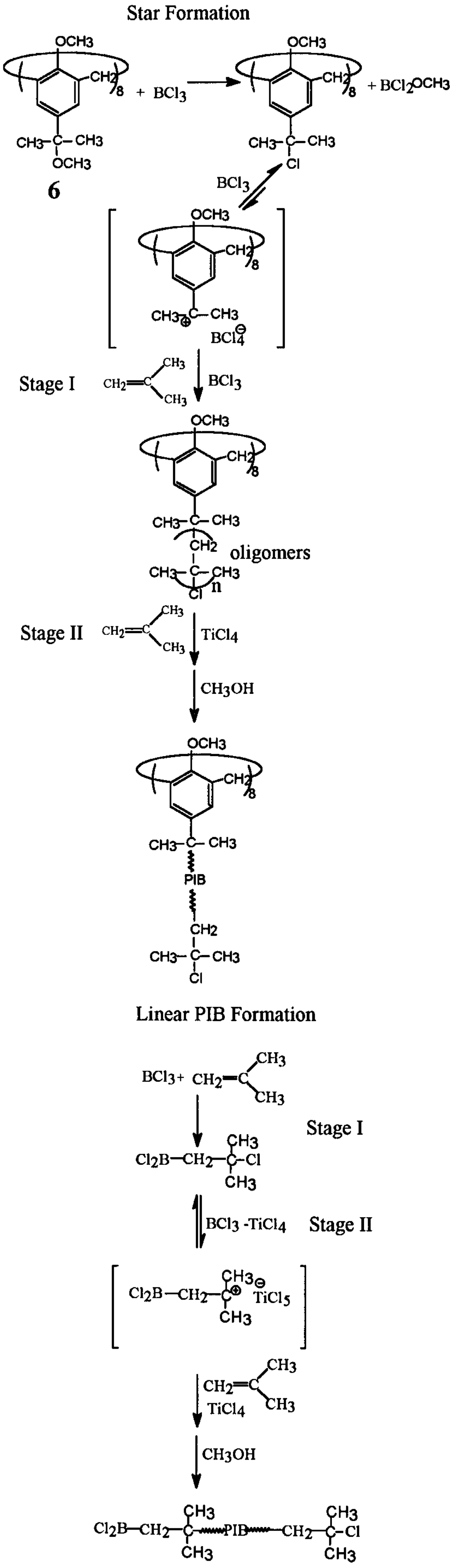


Table 2. Results of IB Polymerization by the Use of 6 as Initiator under Different Conditions[a]

expt no.	initiator, **6** ($M \times 10^3$)	BCl_3 ($M \times 10^2$)	$TiCl_4$ ($M \times 10^2$)	relative amounts[b]		star	
				star	linear	$\bar{M}_w/\bar{M}_n$	comments
1	1.78	47.5	7.45	74	26	1.13	BCl_3 and $TiCl_4$ added in two stages
2	1.78	23.8	7.45	80	20	1.14	BCl_3 and $TiCl_4$ added in two stages
3	1.24	9.90	4.97	81	19	1.14	BCl_3 and $TiCl_4$ added in two stages
4	1.24	4.97	7.94	85	15	1.15	BCl_3 and $TiCl_4$ added in two stages
5	1.08	2.60	7.94	90	10	1.12	BCl_3 and $TiCl_4$ added in two stages
6	1.22	0.993	7.94				BCl_3 and $TiCl_4$ added in two stages, gel formation
7	1.09	2.60	7.94	94	6	1.15	BCl_3 and $TiCl_4$ added simultaneously
8	1.79		22.3				gel formation
9	1.24		11.9				gel formation
10	1.24		7.94				gel formation
11	1.24		5.96				gel formation, low conversion, ∼85%

[a] Concentration of initiating sites, = **6** × 8; [DMA], 2 × (**6** x 8); [DtBP], 1.03×10^{-2} M, −80 °C. Stage I, 60 min; stage II, 45 min (expts 1−6), 50 min (expts 7−11); conversions were ∼100%. [b] Determined by RI peak area (%).

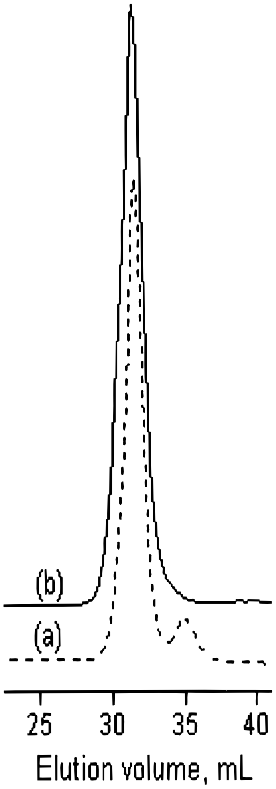


Figure 10. Gel permeation chromatograms: (a) RI trace and (b) UV trace of polymers obtained by using the **6**/BCl_3−$TiCl_4$ initiating system (for conditions, see expt 5, Table 2).

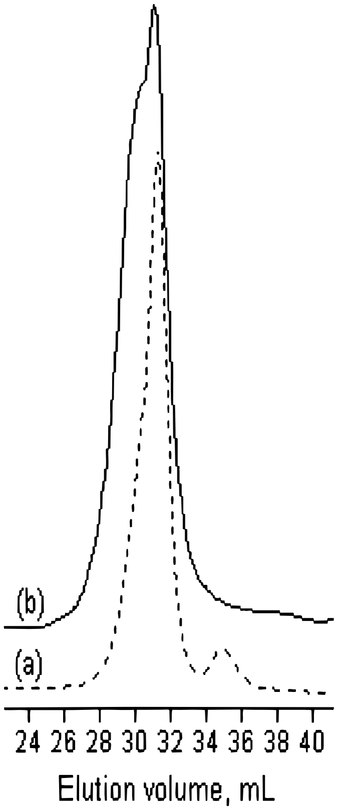


Figure 11. Gel permeation chromatograms: (a) RI trace and (b) UV trace of polymers obtained by using the **6**/BCl_3−$TiCl_4$ initiating system (for conditions, see expt 7, Table 2).

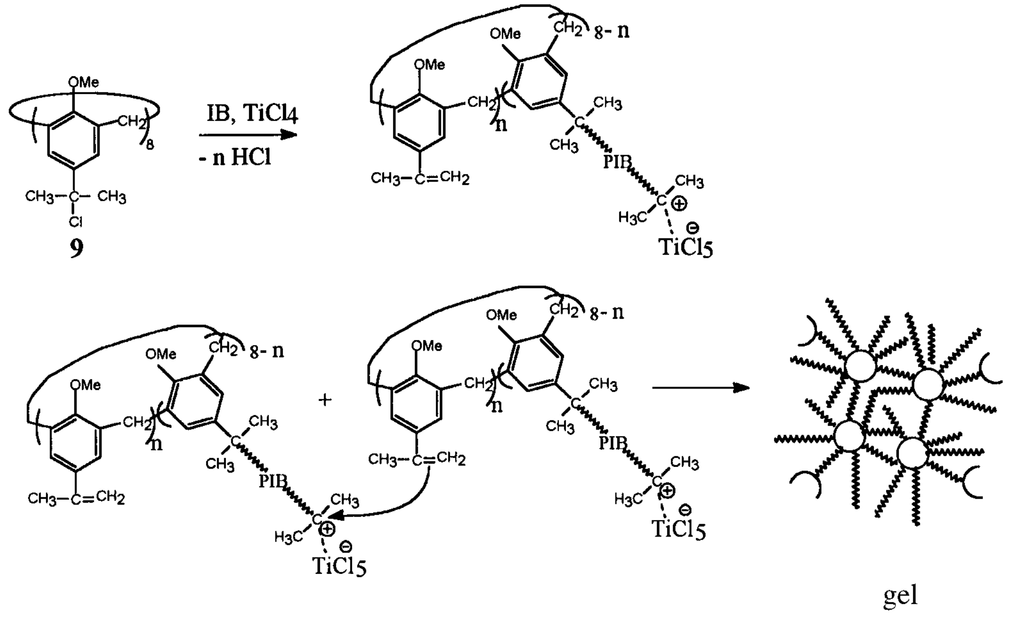
Subsequent experiments were carried out by our two-stage technique with the use of the octafunctional *tert*-ether derivative **6**, which was found to be soluble in CH_3Cl at −80 °C. It was assumed that **6** produces the initiating cation by the transformations shown in Scheme 4.

The $BCl_3OMe^{\ominus}$ counteranion, mainly because of steric compression around the small B center, is even less stable than $BCl_4^{\ominus}$ and rapidly collapses to the *tert*-chlorine derivative, which in conjunction with BCl_3 produces the initiating species. The experiment was carried out by adding BCl_3 to a solution of **6**, adding a partial amount of IB (∼30%) plus other ingredients in CH_3Cl, and reacting the mixture for 90 min. Subsequently the polymerization was completed by the addition of hexanes, $TiCl_4$, and the balance of the IB. Figure 9 shows the GPC (RI and UV) traces of the product. Similarly to the results obtained with **5** (see above), the RI scan shows the presence of two products: the main peak (∼32 mL) is most likely due to the sought star, and the smaller peak (∼37 mL) suggests the presence of ∼26% linear PIB.

The presence of linear PIB in the product prompted systematic investigations into the reduction or elimination of this contaminant. It was theorized that the linear PIB arises either by protic initiation, chain transfer, or initiation by $Cl_2BCH_2C(CH_3)_2Cl$ formed via chloroboration of IB by BCl_3 in stage I. The first two possibilities can probably be excluded in view of the presence of the proton trap in the charge, the low temperatures used, and the carefully dried initiators used.

The clue that $Cl_2BCH_2C(CH_3)_2Cl$ is the source of linear PIB came from control experiments (i.e., experiments carried out in the absence of purposely added initiator **5** or **6**; not reported). According to these studies, the use of BCl_3 and $TiCl_4$ in two stages consistently produced complete IB conversions and

Scheme 6. Route to Gel Formation



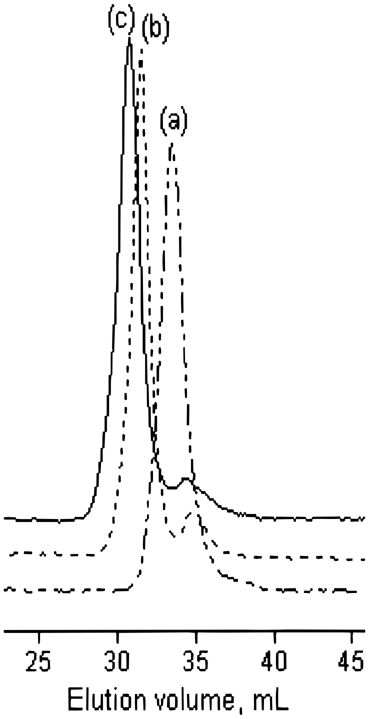


Figure 12. Gel permeation chromatograms (RI traces) of stars with different molecular weights: (a) $\bar{M}_w$(LLS) = 67 000 g/mol; (b) $\bar{M}_w$(LLS) = 115 900 g/mol; and (c) $\bar{M}_w$(LLS) = 273 000 g/mol.

narrow-dispersity PIBs, whereas control experiments with only BCl_3 or $TiCl_4$ (as repeatedly reported[28-30]) gave traces of product or less than 10% conversion, respectively. Also very recently, Faust et al.[31] demonstrated haloboration of IB by BCl_3 under polymerization conditions, similar to those used in this work. Based on these considerations, a series of investigations were carried out in the absence of initiator to elucidate the effects of BCl_3 and monomer concentration in stage I, stage I reaction time, mode of addition of the coinitiators (whether added simultaneously or separately), and $TiCl_4$ concentration on the molecular weight and conversion. Details of these investigations are described elsewhere.[25] In most cases, conversions were ~100%.

Control experiments showed that $TiCl_4$ concentration affects only the rate of polymerization, whereas increasing the BCl_3 and/or monomer concentrations in stage I leads to decreased molecular weight, which suggests the formation of increasing amounts of $Cl_2BCH_2C(CH_3)_2Cl$. In line with these findings, we submit that the polymerizations leading to the sought star and undesirable linear PIB occur by the competing routes shown in Scheme 5.

Thus, the adduct formed by chloroboration of IB is the most likely initiating species for the formation of the linear PIB (see Scheme 5). When $TiCl_4$ is added, rapid polymerization ensues, whereas with only BCl_3, the reaction is limited to mainly chloroboration. The amount of the $Cl_2BCH_2C(CH_3)_2Cl$ depends mainly on BCl_3 and monomer concentrations.

In line with these conclusions, experiments were carried out with **6** using different BCl_3 concentrations, lower amounts of monomer (~25%), and shorter stage I reaction time (60 min). Table 2 shows the data. It was found that, by decreasing the BCl_3 concentration (expts 1–5), the relative amount of the low molecular weight product decreased. With the 0.026 M BCl_3 (expt 5), the amount of the linear PIB dropped to ~10%, the RI and UV traces of the star were symmetrical, and its polydispersity was narrow ($\bar{M}_w/\bar{M}_n$ = 1.11; see Figure 10). At BCl_3 concentrations lower than 0.026 M (expt 6), gel formed (see later). The simultaneous addition of BCl_3 and $TiCl_4$ produced lower amounts of linear product (expt 7; Figure 11), but according to the shoulder in the UV trace, some very high molecular weight stars (~31 mL) also formed conceivably by star–star coupling. Polymerization by the **6**/$TiCl_4$ combination (expts 8–11) also produced gel. A possible route of star–star coupling and ultimately of gel formation is outlined in Scheme 6. Specifically, reactive *p*-isopropenyl groups (which may arise by HCl loss of labile *tert*-chlorine) may intermolecularly attack growing carbocations and thus lead to cross-linking. If the extent of dehydrochlorination is low, star–star coupling may result.

Thus, the two-stage process using low BCl_3 concentrations is the preferred route to the sought stars. In this process, slow propagation in the presence of BCl_3

Table 3. Polymerization Conditions and Molecular Characteristics of Eight-Arm PIB Stars[a]

initiator, **6** (mol x 10^{-5})	IB addition		conv (%)	$\bar{M}_n$(LLS)[b] (g/mol)	$\bar{M}_w$(LLS) (g/mol)	$\bar{M}_w/\bar{M}_n$	$\bar{M}_{n,arms}$ (g/mol)	
	vol (mL)	time (min)					obsd (LLS)	theor[c]
3.18	1	0						
	1.7	60						
		105	~100	62 000	67 000	1.08	7800	6800
3.13	1	0						
	3.4	60						
		105	~100	104 800	115 900	1.11	13 100	11 500
3.16	1	0						
	3.5	60						
	4	80						
	4	105						
		130	~90	244 000	273 000	1.12	30 500	29 000

[a] Concentration of initiating sites, = **6** × 8; [BCl_3], 3 × (**6** × 8); [$TiCl_4$], = 8 × (**6** × 8); [DMA], = 2 × (**6** × 8); [DtBP], 1.03 × 10^{-2} M. [b] Calculated by Astra 4.0. [c] Calculated assuming arm number = 8.

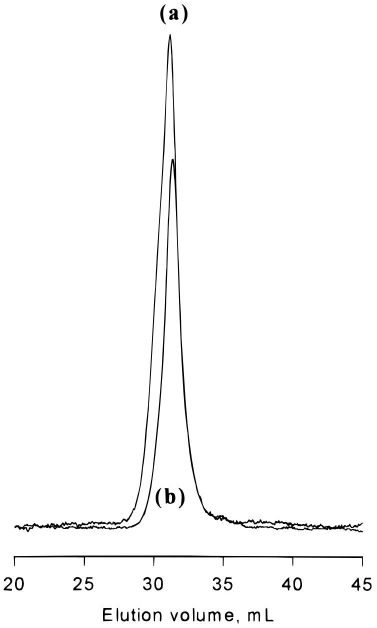
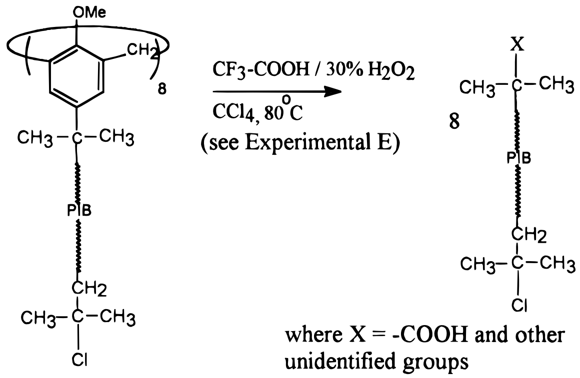


Figure 13. Gel permeation chromatograms: (a) LLS (90°) trace and (b) RI (Optilab 903) trace of star polymer (entry 2, Table 3) after fractionation.

Scheme 7. Core Destruction



where X = -COOH and other unidentified groups

in stage I enables essentially all the initiating sites to add a few IB units, which subsequently grow rapidly in stage II in the presence of $TiCl_4$ to the final product. High molecular weight stars can be prepared by incremental monomer addition. Figure 12 shows the GPC (RI) traces of three select samples with different molecular weights. For the low molecular weight star, only one peak is observed because the peaks associated with the star and the linear PIB overlap. As the molecular weight of the arms increases, the peaks increasingly separate. The relative amount of the linear PIB remains constant (~10%) after two monomer additions, which implies controlled polymerization, i.e., the absence of chain transfer.

Pure star polymer can be readily obtained by removing the linear PIB contaminant by dissolving the mixture in hexanes and precipitating with acetone. Star polymers thus obtained were used for determining the molecular weights by light scattering. Table 3 summarizes select results, and Figure 13 shows the gel permeation chromatograms of a representative sample. Both the LLS (90°) and the RI (Optilab-903) traces indicate the presence of a narrow-dispersity monomodal star. The slight shift of the LLS peak toward higher molecular weights is due to the relatively greater scattering by high molecular weight stars. The d*n*/d*c* of the stars was found to be 0.118 cm^3/g. The $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_w/\bar{M}_n$ of this star were 1.048 × 10^5 g/mol, 1.159 × 10^5 g/mol, and 1.11, respectively. The observed molecular weights of the arms (based on the theoretical number of arms; $\bar{M}_{n,obsd}$ = 13 100 g/mol) were slightly higher than the theoretical value ($\bar{M}_{n,theor}$ = 11 500 g/mol per arm; $\bar{M}_{n,theor}$ calculated after correction for side product), which may be due to less than 100% initiation efficiency and/or overestimation of $\bar{M}_n$.

(c) Determination of the Number of Arms of Star Polymers. NMR spectra and elemental analysis indicate close to eight initiating sites in **6**. To verify our expectation that eight *tert*-methoxy groups in fact gave rise to eight PIB arms, the product of a representative experiment (entry 2, Table 3) was purified (fractionation) and subjected to core destruction. This technique has repeatedly been used in our laboratories to determine the number of arms of star polymers having aromatic cores.[8,15] In core destruction, the aromatic moieties are selectively destroyed by exhaustive oxidation, whereas the saturated aliphatic polymer arms resist oxidation and are quantitated by GPC (see Scheme 7). Experimentally, we found that the core was destroyed after 16 h under the conditions used (single peak by GPC analysis; see Figure 14). Control experiments under similar conditions showed (by GPC) that calixarenes are destroyed by oxidation and form low molecular weight products, whereas linear PIB survives oxidation.

The molecular weight of surviving arms was determined by GPC (LLS) (see Figure 14). The d*n*/d*c* of surviving arms was found to be 0.107 cm^3/g. The $\bar{M}_n$, $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ were 1.366 × 10^4 g/mol, 1.496 × 10^4 g/mol, and 1.23 (by RI), respectively. The distribution of the arms after core destruction was slightly broader than that of the stars. The number-average number of arms, $\bar{N}_{n,arm}$, and the weight-average number of arms,

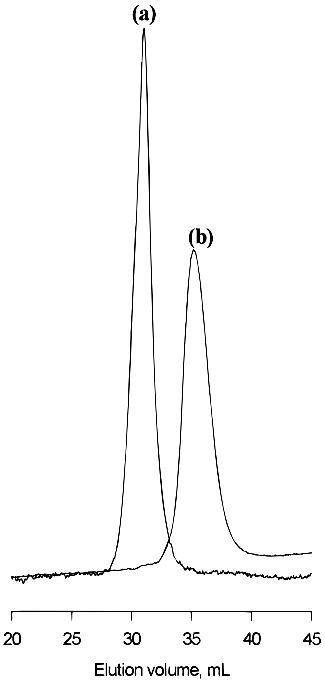


Figure 14. Gel permeation chromatograms (RI traces) (a) before core destruction and (b) after core destruction of star polymers.

$\bar{N}_{\mathrm{w,arm}}$, are $\bar{N}_{\mathrm{n,arm}} = (1.048 \times 10^5$ g/mol $-$ 1536 g/mol)/1.366 $\times 10^4$ g/mol $= 7.6$, and $\bar{N}_{\mathrm{w,arm}} = (1.159 \times 10^5$ g/mol $-$ 1536 g/mol)/1.496 $\times 10^4$ g/mol $= 7.7$. The number of arms was found to be slightly lower than theoretical (i.e., 8.0), which may be due to incomplete initiation and/or incomplete core oxidation. Investigation of the solution properties of these stars is in progress and will be reported later.

Conclusions

The primary objective of this study was the synthesis of novel, well-defined star polymers with eight PIB arms. The goal was achieved with the use of well-defined octafunctional initiators **5** and **6**. IB polymerization studies using these octafunctional initiators revealed that monodisperse PIB stars can be prepared using BCl_3-TiCl_4 coinitiators by a two-step process in the presence of DMA and DtBP. High molecular weight stars were prepared by the IMA technique. Determination of the number of arms by core destruction indicated close to the theoretical number of arms, i.e., 8. The utility of these octafunctional initiators can be extended to the synthesis of block stars, end-functionalized stars, etc.

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