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Synthesis and characterization of a novel octa-arm polyisobutylene star*

A. F. Moustafa[1], S. A. Yankovski, J. P. Kennedy

Maurice Morton Institute of Polymer Science, The University of Akron, Akron, OH 44325-3909, USA
[1]Permanent Address: National Research Center, Polymer Department, Cairo, Egypt

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Summary

The synthesis and characterization of a novel telechelic star consisting of a well defined C-pentyl-calix[4]1,3-dicumyl alcoholarene **(3)** core out of which radiate eight well-defined polyisobutylene arms, each fitted with an allyl terminus is described. The synthesis was accomplished by a core-first method, by inducing the living polymerization of isobutylene by **3** in conjunction with BCl_3-$TiCl_4$ coinitiators. The product was characterized by GPC coupled with laser light scattering (LLS) and referactive index (RI) detectors, and by ^1H NMR spectroscopy. Quantitative functionality analysis indicated the presence of exactly eight PIB arms per molecule.

Introduction

Kennedy et al.[1,2] were the first to describe the synthesis of a well defined telechelic star consisting of a calix[8]arene core out of which radiate eight terminally functional PIB arms. While the polymerization phase of the synthesis was readily effected, the preparation of the octafunctional initiator 5,11,17,23,29,35,41,47-(2-methoxypropyl)-49-50,51,52,53,54,55,56-octamethoxy calixarene was cumbersome as it involved eight steps and, consequently, gave poor yields[1]. In the course of our investigations focusing on octa-arm PIB star crosslinking agents, we have developed a simple, high yield, three step synthesis for the preparation of a novel octafunctional initiator, **3**, which in conjunction with BCl_3, readily mediates the living polymerization of IB and produces well-defined cationic polymerization of IB and well-defined octa-arm stars.
This article concerns details of the synthesis of the initiator and that of the octa-telechelic star, together with the characterization of these entities by a variety of techniques.

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* This is part XXVII in the series *Novel Polyisobutylene stars*. For part XXVI in this series see D. H. Hull and J. P. Kennedy, J. Polym. Sci., Part A: Polym. Chem, Vol. 39, 1525 (2001)

Experimental

Materials

Resorcinol (99%), hexanal (99%), ytterbium triflate Yb(OTf)3, di-*tert*-butylbiphenyl, methyl iodide (99%), NaH, $TiCl_4$, dimethylacetamide (DMA), di-*tert*-butylpyridine, (D*t*BP), $CD_2Cl_2$and $CDCl_3$ were from Aldrich and were used as received. Isobutylene (IB, CP grade) and methyl chloride were from Matheson. The gases were dried by passing them through columns packed with BaO, Drierite, Molecular Sieves, and $CaCl_2$. Hexanes and THF were refluxed overnight over CaH_2 and distilled before use.

Synthesis of C-pentyl-calix[4]resorcinarene[3-6] 1.

A solution of resorcinol (11g, 0.1 mole) and hexanal (0.1 mole) in absolute ethanol (250 mL) was stirred under reflux in the presence of $Yb(OTf)_3$ (5 g, 8 mmol) for 48 h. The resulting product was precipitated into distilled water (300mL) and filtered. The yellow product **1** was dried in a vacuum oven at 100 °C for 24 h. Recovered yield was 95% of pale yellow crystals. The catalyst was recovered from the filtrate and dried in a vacuum oven for 48h for reuse.

Synthesis of C-pentyl-calix[4]1,3-dimethoxy benzenarene 2.

1 (12g, 10.8 mmol) was dissolved in THF (200 mL) and sodium hydride (1.334g, 55.6 mmol) was added in small amounts to the stirred solution. After the hydrogen evolution ceased, methyl iodide (6.8 ml, 21 mmol) was added dropwise and the stirred mixture was refluxed for 24 hours. **2** was extracted with diethyl ether, dried over magnesium sulphate for 24 h and the ether was removed by a rotary evaporator. **2** a yellow gelatinous mass, was dried in a vacuum oven at room temperature for one week. The recovered yield of the final yellow solid product **2** was 90 %. Mp = 90 °C.

Synthesis of C-pentyl-calix[4]1,3-dicumyl alcoholarene 3.

For the synthesis of **3,** we have modified the procedure by Bachi et al. and Foubleo et al.[7,8]. Thus a suspension of **2** (3g, 3.3 mmol) in THF (200 mL) was stirred with 14 times molar excess of metallic lithium (0.32g, 46.2 mmol). A stochiometric amount of di-*tert*-butylbiphenyl was added to the charge and stirred at room temperature for 4 hours. The mixture was cooled to – 40 °C, acetone (20 mL) was added dropwise followed by distilled water (10 mL). The charge was filtered to remove the unreacted lithium. The yellow crystalline product was extracted with chloroform and recrystallized three times from chloroform/methanol (80/20v/v). The final recovered yield of **3** was 90%.

Polymerization of Isobutylene by 3

Polymerizations were carried out in two stages following published procedures[9]. In a 2L three neck round bottom flask equipped with a mechanical stirrer in a dry box at – 80 °C, initiator **3** (1.104 g, 1 mmol) was dissolved in CH_3Cl (320 mL), and then in sequence DMA (1.38mL, 16 mmol), D*t*BP (1.79 mL, 8 mmol), IB (70mL, 898 mmol), and hexane (360 mL) were added. Polymerizations were induced by the addition of

BCl_3 (7.6 mL, 24 mmol). After 1 h, $TiCl_4$ (7ml, 64 mmol) in prechilled hexane (60 mL) was added. After 1 h of stirring, prechilled ATMS (25ml, 157 mmol in 50 mL hexane) was added and the charge was stirred for 30 minutes. Finally the polymerization was quenched with prechilled methanol (50 mL). The solvents were allowed to evaporate over night. The star PIB was redissolved in hexanes and washed several times with water, three times with methanol and finally several times with distilled water until the solution became clear. The PIB star solution was dried over magnesium sulphate for 24 h, filtered and the solvent was removed by a rotary evaporator.

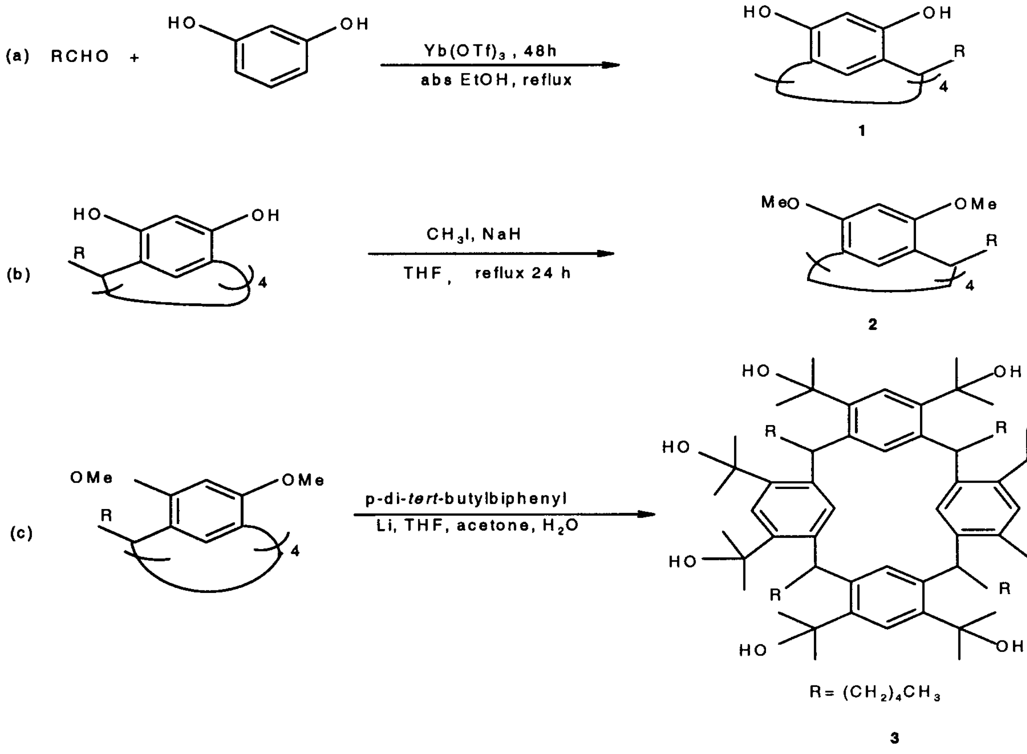

Fig. 1 Synthesis of C-pentyl-calix[4]1,3-dicumyl alcoholarene **3**

Gel Permeation Chromatography

A Waters GPC instrument equipped with a refractive index detector (Waters 410 Differential Referactometer) and a laser light scattering (LLS) detector (Wyatt Technology) operating with Astra software (Version 4.0, Wyatt Technology) was used. The flow rate was 1mL, of THF/min. Details of the procedure have been described[10,11].

Nuclear Magnetic Resonance Spectroscopy

Proton NMR spectra of the initiator **3** and the silylated PIB were recorded with a Varian Gemini-300 MHz “nmr5” spectrometer at ambient temperature. Samples were prepared in 5 mm diameter sample tubes with ~ 20 mg/mL of $CDCl_3$ or CD_2Cl_2. The details of the method have been described[10,12].

Results and discussion

Synthesis and charcterization of 3

According to our search of the scientific and patent literature, **3** has not yet been described, and it certainly was not used to mediate cationic polymerizations. Figure 1 outlines the synthesis of **3** and the structures of the intermediates. The synthesis of **3** involves the condensation of resorcinol and hexanal, followed by the nucleophilic attack of the lithium calixoxide on the carbonyl group of acetone to form the tertiary alcohol.

In a previous publication[1], we described the use of a methoxy derivative of calix[8]arene to initiate the cationic polymerization if IB. In line with this experience[1] we thought that the methoxy derivative of **3** will be our preferred initiator. However, solubility studies indicated that this $-OCH_3$ derivative was sparingly soluble in CH_2Cl_2 and $CHCl_3$ and insoluble in hexanes. In contrast, **3** was found to be soluble in CH_2Cl_2, $CHCl_3$ and $CHCl_3$/hexanes (80/20 v/v) mixture, and sparingly soluble in hexanes. In view of these solubility studies we decided to use CH_3Cl/hexanes solutions of **3** for our polymerizations experiments (see Experimental).

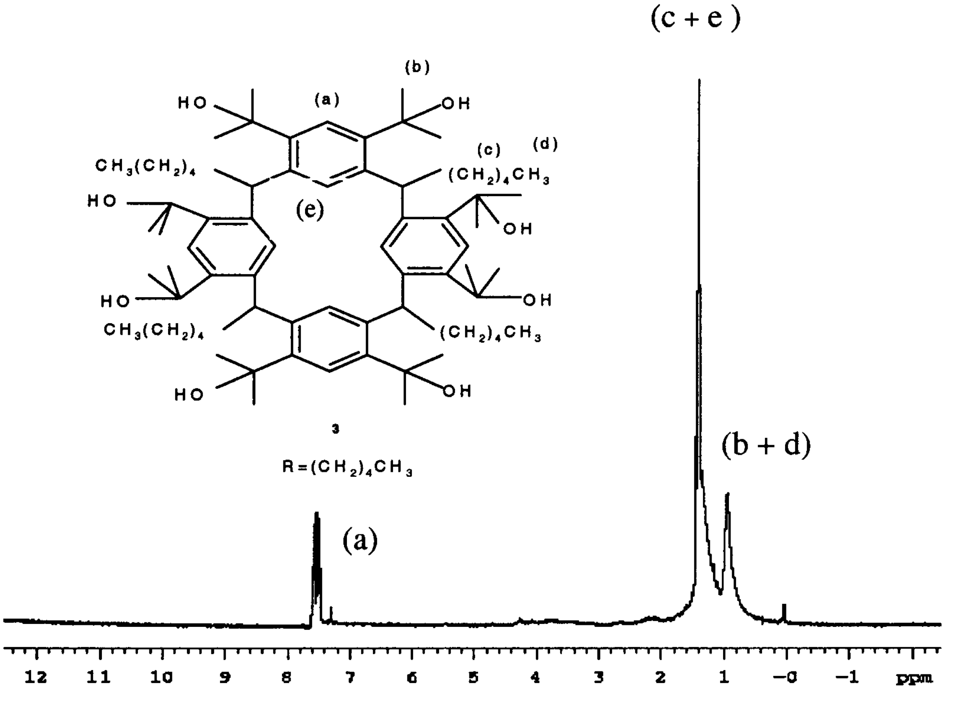

Fig. 2 ^{1}H NMR Spectrum of C-pentyl-calix[4]1,3-dicumyl alcoholarene **3**

The structure of **3** was investigated by ^{1}H NMR spectroscopy. Figure 2 shows the ^{1}H NMR spectrum of recrystallized **3**. The multiplet at 7.5 ppm represents, the unsubstituted eight aromatic protons (a) in the box and chair conformations[6] of **3**. The peak at 0.8 ppm is associated with the methyl protons (b and d) while the methylene and the methine protons (c and e) appear at 1.2 ppm. Figure 3 shows the FT-IR spectrum of **3**. The OH function is indicated by the absorption of 3411 cm^{-1}.

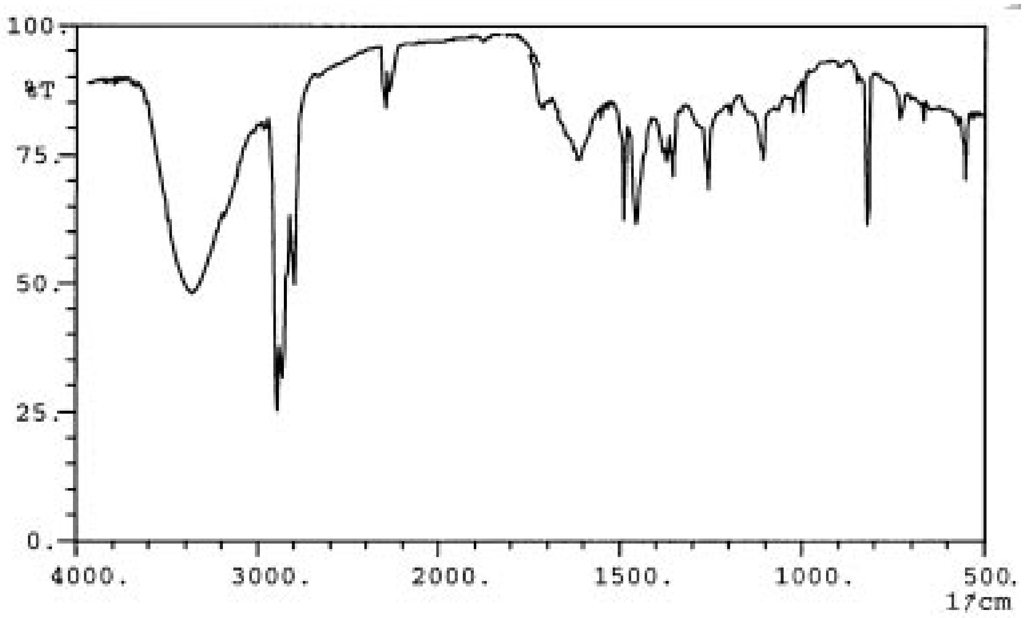

Fig. 3 FT-IR Spectrum of 3

Isobutylene polymerization and characterization of PIB

According to extensive previous experience in our laboratories, living IB polymerizations can be readily mediated by calix[8]arene/BCl_3-$TiCl_4$ initiating systems[1,2]. In line with this background, we have used **3**/BCl_3-$TiCl_4$ combinations to initiate IB polymerizations.

Figure 4 outlines the synthetic steps leading to the octa-trimethylsilyl-telechelic star, C[4](PIB-$SiMe_3)_8$. No efforts have been made to isolate the intermediates because ample published evidence exists which demonstrates the quantitative nature of the transformations indicated (see references 12, 13 and 14).

Figure 5 shows the ^{1}H NMR spectrum of C[4](PIB-$SiMe_3)_8$. Integration of the 72 -$SiMe_3$ protons at 0.1 ppm relative to the eight unsubstituted aromatic protons at 7.2 ppm in the initiator fragment yields F_n =8.12. According to this evidence, the number of PIB arms radiating from the C[4] core is close the theoretical value of 8.

The homogeneity and molecular weight of the eight-arm PIB star was investigated by GPC. Figure 6 shows the RI and LLS traces of a representative product. The RI trace shows a major peak associated with the star (~32 mL elution volume) of M_n/M_w = 1.2, a very small peak at ~ 44 mL that is most likely due to homo PIB produced by

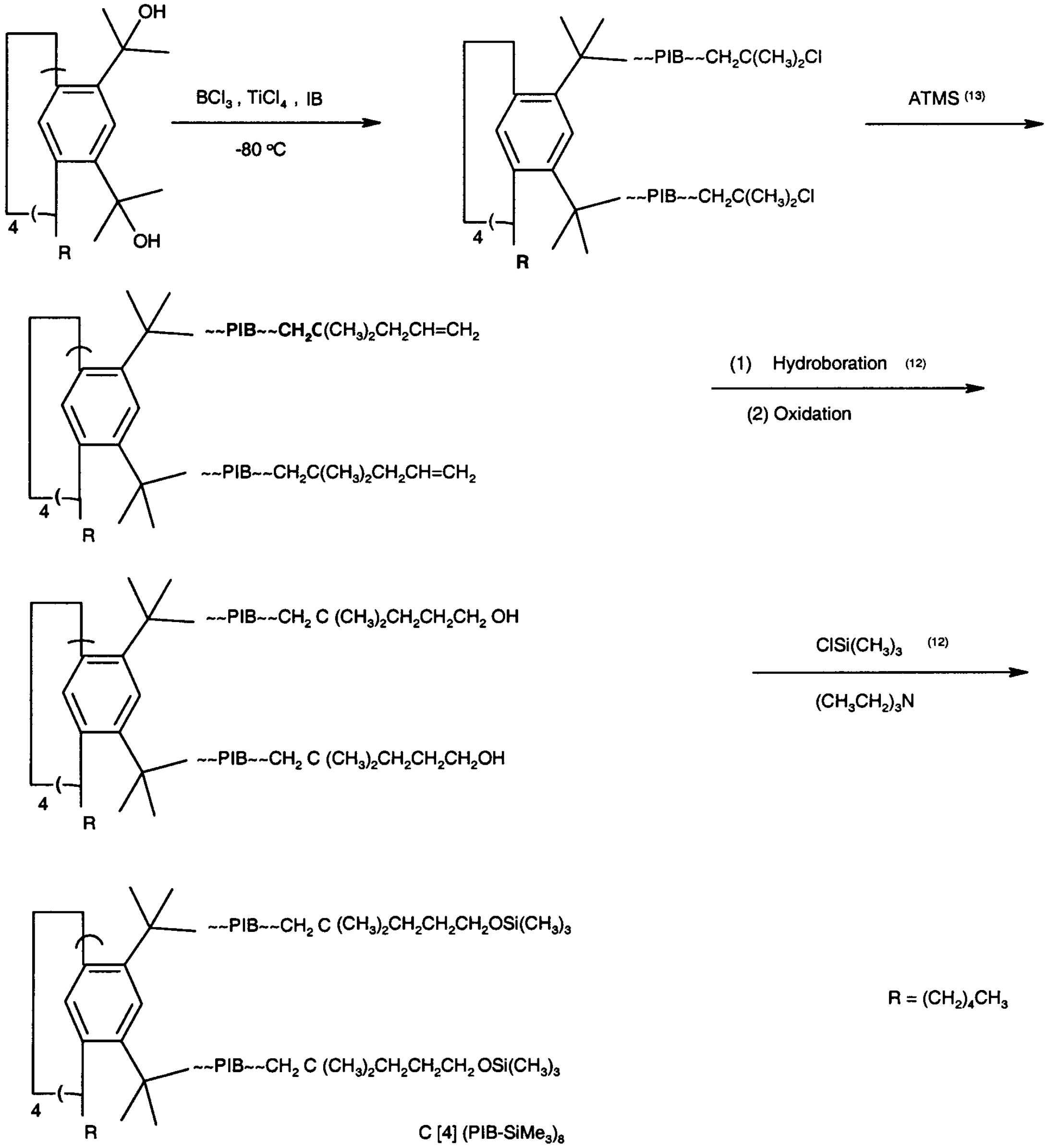

Fig. 4 Scheme of IB Polymerization and End-Functionalization of PIB arms

ubiquitous moisture in the charge, and a sharp peak at ~ 47 mL due to unreacted **3**. The LLS trace exhibits only one sharp peak at ~ 32 mL associated with the star and indicates a Mw of ~ 60,000 g/mol. Due to the limited solubility of **3** in the polymerization charge, a portion of the initiator remained unreacted and because of this deficit the molecular weight of the star was higher than the expected value.

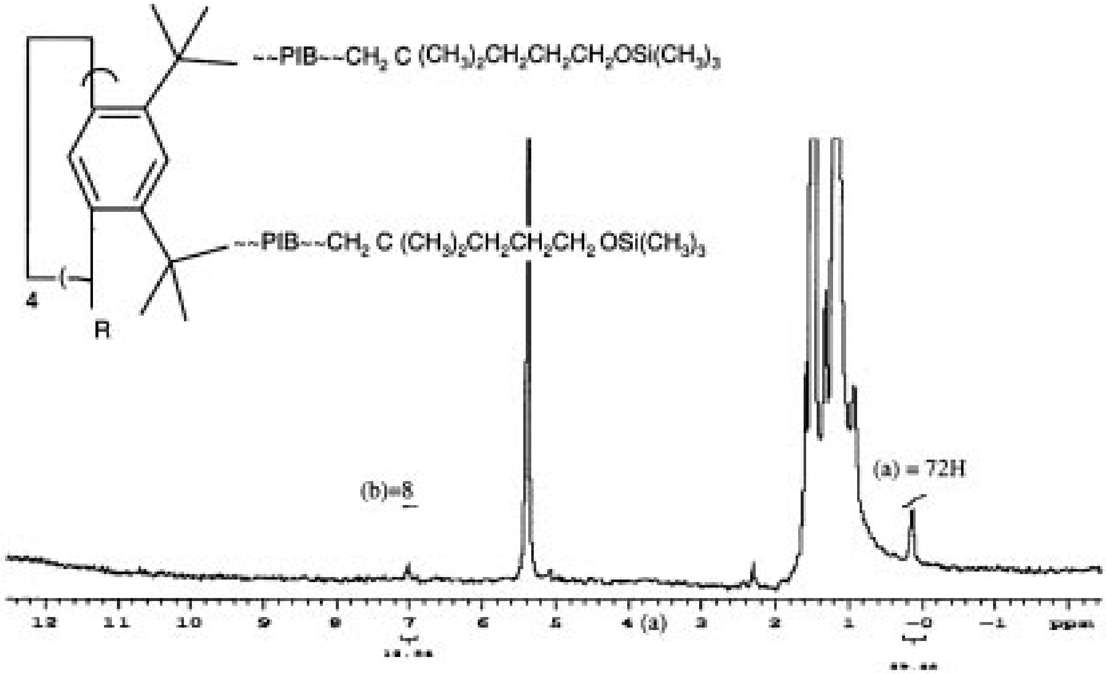

Fig. 5 ^{1}H NMR Spectroscopy of octa-arm star C[4](PIB-SiMe$_3$)$_8$

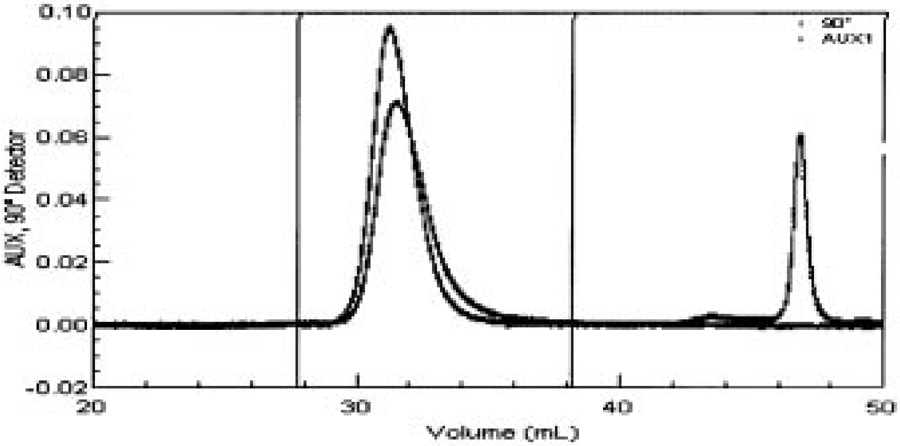

Fig. 6 GPC traces of an octa-arm star: a) RI detector; b) LLS detector

Conclusions

A new octafunctional initiator for cationic polymerization, C-pentyl-calix[4]1,3-dicumyl alcohoarene, **3**, was prepared in high yield in three simple steps. Characterization by ^{1}H NMR spectroscopy proved the octa-functional structure. Polymerization of isobutylene induced by **3** in conjunction with BCl_3-$TiCl_4$ coinitiators gave novel stars consisting of a calix[4]arene core out of which radiate eight PIB arms. A series of quantitative functionalizations of the outer ends of the PIB arms led to octa-trisilyl-telechelic PIB stars. The microstructure of the octa-arm stars was established by quantitative ^{1}H NMR spectroscopy.

Acknowledgements.

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