# New polyisobutylene stars

## XI. Synthesis and characterization of allyl-telechelic octa-arm polyisobutylene stars *

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## Abstract

The synthesis and characterization of a novel star comprising eight allyl-terminated polyisobutylene (PIB) arms radiating from a calix[8]arene core is described. The synthesis was accomplished by a core-first method, by inducing the living polymerization of isobutylene (IB) by a suitably functionalized calix[8]arene initiator (**1**) in conjunction with $BCl_3$-$TiCl_4$ coinitiators, and terminating the growth of the living $PIB^{\oplus}$ arms by allyltrimethylsilane. The relative concentrations of $BCl_3$ and $TiCl_4$ are critical for the synthesis of well-defined 8-arm stars. Characterization of the products (which included triple detector GPC studies and $^1H$ NMR spectroscopy) indicated quantitative allylation. A mechanism which summarizes the experimental observations is proposed.

## Introduction

As part of our ongoing research on the synthesis of useful and novel isobutylene (IB)-based stars [1], we became interested in the preparation of well-defined multi-arm star polyisobutylenes (PIB) carrying functional groups at the end of the arms. The synthesis by a core-first strategy of well-defined octa-arm PIB stars by the use of the octafunctional initiator 5,11,17,23,29,35,41,47-(2-Methoxypropyl)-49,50,51,52,53,54,55,56-octamethoxycalix-[8]arene (1) in conjunction with $BCl_3$-$TiCl_4$ coinitiators has been reported [2,3]. Here we give new insight into: (**1**) the conformation of the initiator **1** generated by computer modeling, (ii) the use of $BCl_3$ for initiation (Stage I) and subsequent use of $TiCl_4$ after the start of the polymerization (Stage II) for the synthesis of monomodal narrow dispersity *tert*-Cl end-capped octa-arm stars, and (iii) the versatility of the core-first approach for the preparation of allyl-functionalized octa-arm stars.

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\* For paper X of this series see S. Asthana, I. Majoros, and J. P. Kennedy, Polym. Mat. Sci. Eng., <u>77</u>, 187 (1997).
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## Experimental

### Materials

The materials for the synthesis of initiator **1** as well as for stars comprising a calix[8]arene core and eight PIB arms capped by *tert*-Cl have been described [2,3]. Allyltrimethylsilane (ATMS) (Aldrich) was used as received.

### Preparation of Allyl Functionalized Octa-arm PIB Stars by the Use of the **1**/BCl$_3$-TiCl$_4$ Initiating System

The overall methodology of IB polymerization by a two-stage procedure has been described [2]. The terminal allyl-functionalization of the living PIB$^\oplus$ arms was carried out by adapting a procedure developed in our laboratories [4]. Stock solutions of initiator, dimethyla-cetamide (DMA), di-*tert*-butylpyridine (DtBP), and BCl$_3$ were prepared in CH$_3$Cl, and TiCl$_4$ in hexanes. In Stage I, the addition sequence of the reactants was: initiator (**1**), CH$_3$Cl, IB (1 mL), DMA, DtBP, and BCl$_3$. After polymerizing for 60 minutes, hexanes, TiCl$_4$, and the balance of IB were added. The ultimate CH$_3$Cl:hexanes ratio (v/v) was 40:60. ATMS (~ 100 fold excess relative to the PIB$^\oplus$ chain end) was added when IB conversions reached ~95%. After 60 minutes the charge was poured into an excess of chilled methanol, the product separated, redissolved in hexanes, washed with water and methanol, and finally reprecipitated into methanol. See also first footnote under Table 1.

### Characterization

$^1$H NMR spectra (~30 mg sample in CDCl$_3$)were recorded by a Varian Gemini-300 (with 10 000 FIDs) or Varian-600 (64 FIDs) spectrometer using standard 5 mm tubes at room temperature. Molecular weights were determined by GPC (Waters Co.) equipped with a series of five μ -Styragel columns (100, 500, 10$^3$, 10$^4$, and 10$^5$), a RI detector (Waters 410 Differential Refractometer), a UV detector (440 Absorbance Detector), and a laser light scattering (LLS) detector (Wyatt Technology). The methodology has been described [2]. The dn/dc values were obtained by using an Optilab 903 (Wyatt Technology) instrument as specified [2]. The number of arms were determined by core-destruction [2]. Modeling studies were carried out by using a CS Chem 3D software. The energy minimizations were based on MM2 force field with an RMS gradient of 0.001.

## Results and Discussion

### A. Computer Modeling of **1**

The synthesis of initiator **1** involved the introduction of -C(CH$_3$)$_2$OCH$_3$ groups at the 'upper-rim' of 5,11,17,23,29,35,41,47-octaacetyl-49,50,51,52,53,54,55,56-octamethoxy-calix[8]arene [2]. Figure 1 (a) and (b) show structural formula of **1** and the minimum energy structure generated by computer modeling, respectively. The three-dimensional structure obtained by modeling shows that the initiating methoxy sites in **1** are sterically unhindered. The molecule possesses an ellipsoidal shape with a preferred 1,2 alternate arrangement for the aryl rings. The $^1$H NMR spectrum of **1** [2] showed a broad singlet for methylene bridge

**1**

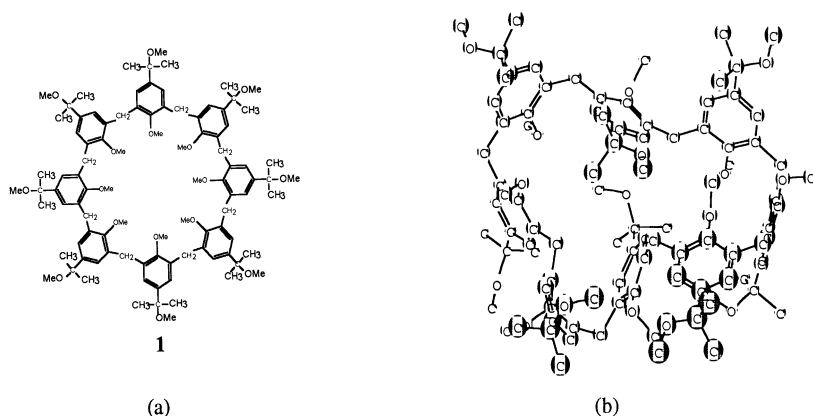(a)                                                         (b)

Fig. 1. Structure of initiator **1**: (a) two-dimensional structure; (b) minimum energy structure
(hydrogen atoms omitted).

protons which is indicative of rapidly interconvertible conformations [5]. The quantitative
functionalization of the 'upper-rim' is critical for the preparation well-defined octa-arm stars by
**1**.

### B. The Effect of $BCl_3/TiCl_4$ Ratio on Product Uniformity

Results of earlier research [7,8] on IB polymerization with $BCl_3$-$TiCl_4$ mixtures greatly
helped our efforts to find conditions for the synthesis of well-defined PIB stars by **1**.
Similarly to previous results, we have found that the $BCl_3/TiCl_4$ ratio controls the outcome of
the synthesis, however, in contrast to earlier work in which premixed $BCl_3/TiCl_4$ systems were
used [8], desirable narrow dispersity products formed only when the $BCl_3$ and $TiCl_4$
coinitiators were added in sequence in two-stages and only in the presence of well-chosen
$BCl_3$-$TiCl_4$ concentrations [2]. The data in Figure 2 illustrate the criticality of $BCl_3$ and $TiCl_4$
concentrations. $TiCl_4$ alone leads to gel and /or multimodal products (see Fig. 2 (a)-(c)). The
use of too low $TiCl_4$ concentrations yields low conversions (~25%) and broad molecular
weight distribution products (Fig. 2(a)). By increasing the $TiCl_4$ concentration, higher
conversions can be obtained, however, the products are ill-defined and contain gel (Fig. 2 (b)-
(c)). Similarly unsatisfactory results were obtained either by the use of mixed $BCl_3/TiCl_4$
systems or when insufficient amounts of $BCl_3$ were used in conjunction with $TiCl_4$ in two
stages (Fig. 2(d)).

In contrast, well-defined narrow dispersity stars, $\overline{M}_w/\overline{M}_n = $~1.1, can be prepared by
inducing the polymerization with relatively higher concentrations of $BCl_3$ and $TiCl_4$ used in
sequence. For example, by the use of ~0.026 M $BCl_3$ (Stage I) and continuing the reaction by
the addition of ~0.079 M $TiCl_4$ (Stage II) gave monomodal narrow dispersity product (see Fig.
2(e)) [2,3]. Evidently, in this system the sequential addition of $BCl_3$ and $TiCl_4$ is necessary to
obtain desirable product characteristics (this aspect of our findings is further discussed in
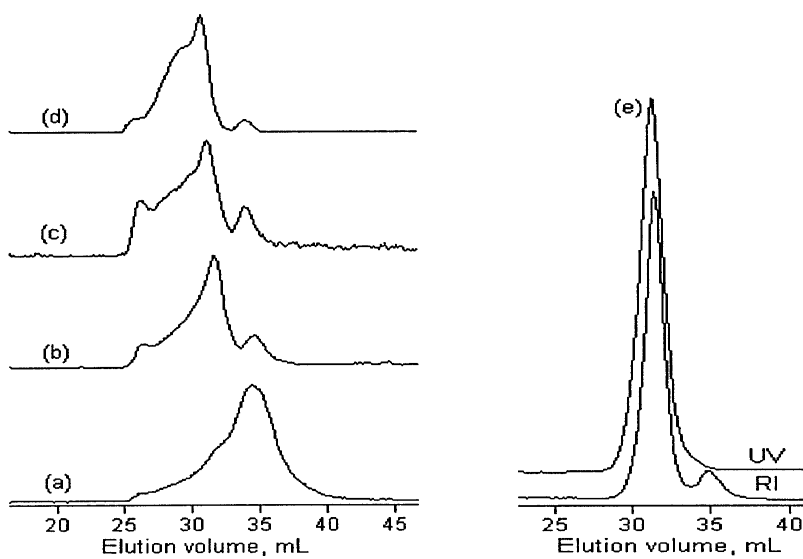Section D).

Fig. 2. GPC (RI) traces of products obtained at different coinitiator concentrations (in M) BCl$_3$/TiCl$_4$: (a) 0/0.059; (b) 0/0.079; (c) 0/0.12; (d) 0.01/ 0.079; (e) 0.026/0.079.



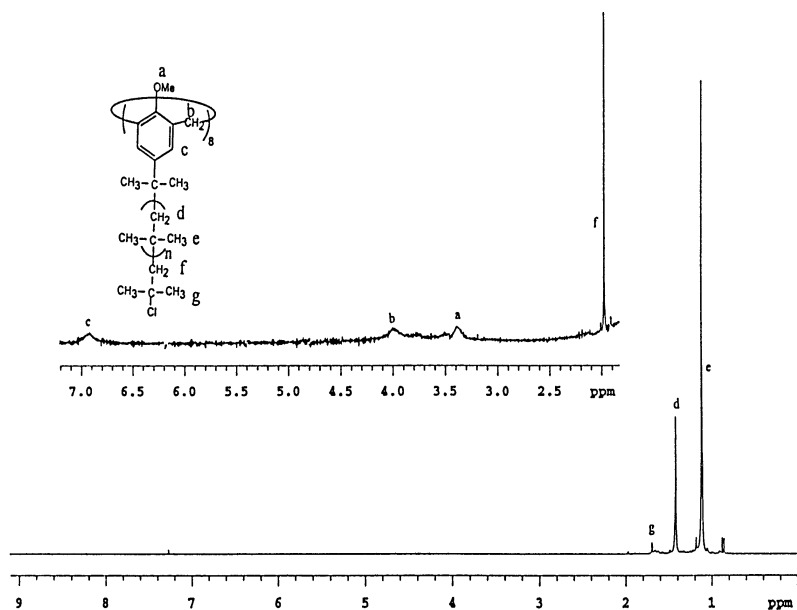Fig. 3. $^1$H NMR (300 MHz) spectrum of *tert*-Cl end-capped octa-arm PIB star ( $\overline{M}_w$ = 3.76x10$^4$ g/mol) containing a calix[8]arene core.

*C. Characterization of Stars.*

The PIB stars were characterized by GPC (triple detector), $^1$H NMR spectroscopy, and core-destruction experiments [2]. GPC(LLS) results showed the formation of stars having molecular weights slightly higher than theoretical values. Core-destruction [2] experiments indicated the presence of number of arms close to the theoretical value of 8. To facilitate the interpretation of $^1$H NMR spectra, low-molecular weight stars were prepared. Figure 3 shows the $^1$H NMR spectrum of a virgin sample indicating resonances at $\delta$=1.95 and $\delta$=1.65 ppm, characteristic of protons of the terminal -CH$_2$-C(CH$_3$)$_2$-Cl group [8]. Absence of resonances at $\delta$~4.6 and $\delta$~4.8 ppm characteristic of terminal unsaturation further indicates that the arms carry *tert*-Cl end groups. The functionality of the star was calculated by comparing the integrated peak area of core protons (aromatic ($\delta$=6.8 ppm), -CH$_2$- ($\delta$=4.0 ppm)) to the chain end protons (-CH$_2$- ($\delta$=1.95 ppm), and -CH$_3$ ($\delta$=1.65 ppm)). This procedure gave ~8.1 arms per core, after correcting for the presence of ~10% linear contaminant (see Fig. 2(e), ~35 mL); the origin of this contaminant has been explained [2]. Specifically, the origin of this linear product is believed to be polymer which arose by the Cl$_2$BCH$_2$C(CH$_3$)Cl, which in turn arose by chloroboration of IB by BCl$_3$. Thus $^1$H NMR spectroscopy provides direct proof for the formation of the sought *tert*-Cl telechelic octa-arm stars.

*D. Mechanism of Star Synthesis by BCl$_3$-TiCl$_4$ Coinitiators*

The experimental observations can be explained by the mechanism shown in Scheme 1 together with the following discussion: The initial event is the formation of **2** from **1** (under the influence of BCl$_3$ or TiCl$_4$ [9]) which in the presence of excess BCl$_3$ gives **3**. The existence of an equilibrium between dormant and active species such as **2** and **3** in living IB polymerization has been discussed in detail [9]. The ionicity of the active form **3** and its position in the Winstein spectrum [9] depend on experimental conditions (i.e., nature and concentration of the coinitiator, additives (e.g., organic bases), temperature, solvent polarity, etc.). During Stage I of the polymerization the active intermediate **3** undergoes slow propagation by route ⓞ to give stars with oligomeric arms. The equilibrium ⑪ between the living **3** and dormant **2** is rapid with the dormant species **2** predominating. Thus the symbol **2** stands not only for the initially formed *tert*-benzylic chloride (shown) but also for stars carrying relatively low molecular weight *tert*-chlorine ended PIB arms [i.e., **1**(~~~~-CH$_2$-C(CH$_3$)$_2$-Cl )$_8$]. The reverse reaction of ⑪ is very rapid due to the highly unstable BCl$_4$ $^\ominus$, thus deprotonation of **3** or the deprotonation of the equivalent low molecular weight stars **1**(~~~~-CH$_2$-C(CH$_3$)$_2$$^{\delta\oplus}$ --- BCl$_4$$^{\delta \ominus}$ )$_8$ are absent.

Stage II starts with the introduction of TiCl$_4$ which rapidly converts dormant **2** into active species **4** which in turn undergoes relatively fast propagation by ⓒ; the rate of ⓒ is higher than that of ⓞ. Also competing with ⓒ is rapid counter anion exchange by path ⑪ [(TiCl$_5$$^\ominus$ + BCl$_3$ $\rightleftharpoons$ TiCl$_4$+ BCl$_4$$^\ominus$ ) [7]] which converts 4 via 3 to the dormant from **2**.

In the course of Stage II, processes ⑪ → ⓒ → ⑪ → ⑪ occur in rapid succession and produce the sought stars with *tert*-chlorine ended PIB arms. During Stage II propagation via ⓞ is relatively unimportant. Also the extent of deprotonation (process ⓓ ) is negligible because the rate of this process is low relative to processes ⑪ and ⓒ [7]. Hence BCl$_3$ serves two purposes: (i) it ensures complete initiation in Stage I, and (ii) it stabilizes the chain end in Stage II by reducing the life-time of the relatively long-lived PIB$^\oplus$TiCl$_5$$^\ominus$ ) ion-pairs through counter anion exchange, and thus rapidly produces stars with tert-Cl end functionalized arms [i.e., 1(~~~~~~-CH$_2$-C(CH$_3$)$_2$-Cl )$_8$].
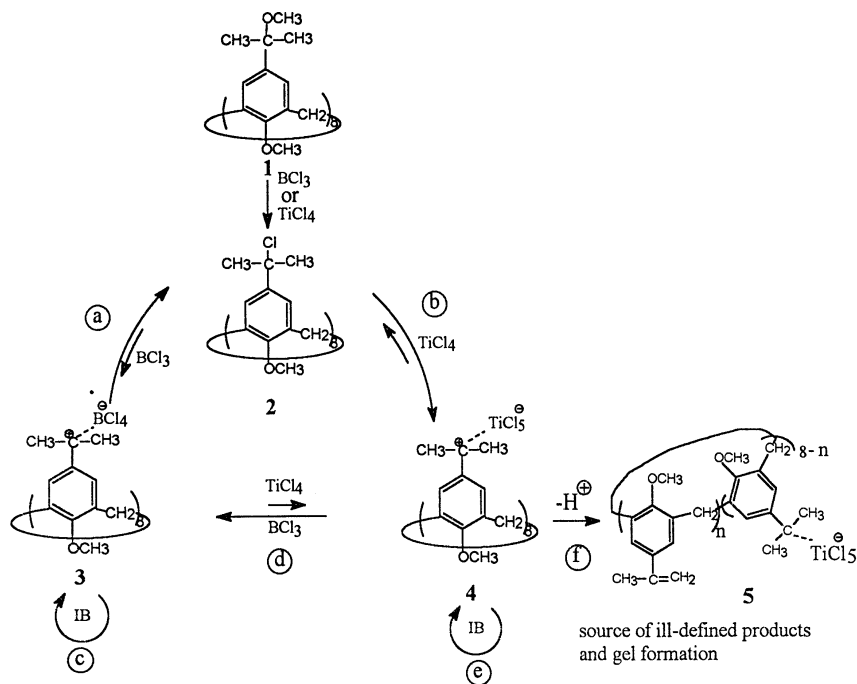
Scheme 1. Mechanism of Synthesis of *tert*-Cl Telechelic PIB Stars by the Use of BCl$_3$-TiCl$_4$ Coinitiators.

In contrast, if TiCl$_4$ is used alone the polymerization proceeds only by ⓑ → ⓒ and ⓕ. Since TiCl$_5^{\ominus}$ is more stable than BCl$_4^{\ominus}$ [7], active intermediate **4** is longer lived than **3**, and will undergo facile proton elimination (process ⓕ) to form undesirable structures akin to **5** having α-methylstyrene-type groups. Similar isopropenyl-terminated structures may also arise from growing PIB$^{\oplus}$ arms by proton elimination (chain transfer). Copolymerization of such double bonds during star formation will lead to high molecular weight stars and/or gel. The broad molecular weight products and/or gels observed even at low IB conversions (~25%) indicate that they form primarily due to the interaction of **5** with growing PIB$^{\oplus}$ arms during star formation.

*E. Synthesis and Characterization of Allyl-Telechelic Octa-arm Stars*

Scheme 2 shows the steps involved in the synthesis. The stars were characterized by GPC and $^1$H NMR spectroscopy. According to $^1$H NMR evidence (Fig. 4) the arms were quantitatively functionalized with allyl groups. The end-functionality of the stars was calculated by comparing the integrated peak area of the core protons (aromatic ($\delta$= 6.82 ppm), -CH$_2$-($\delta$= 4.0 ppm)) and chain end allyl protons (-CH$_2$-($\delta$= 2.0 ppm), -CH=($\delta$= 5.8 ppm), =CH$_2$ ($\delta$= (5.1 ppm), and was found to be 8.1, after correcting for the presence of ~10% linear contaminant. Quantitative allyl-functionalization is direct proof for the formation of the sought octa-arm stars. Molecular characteristics of two representative samples are summarized in Table 1.
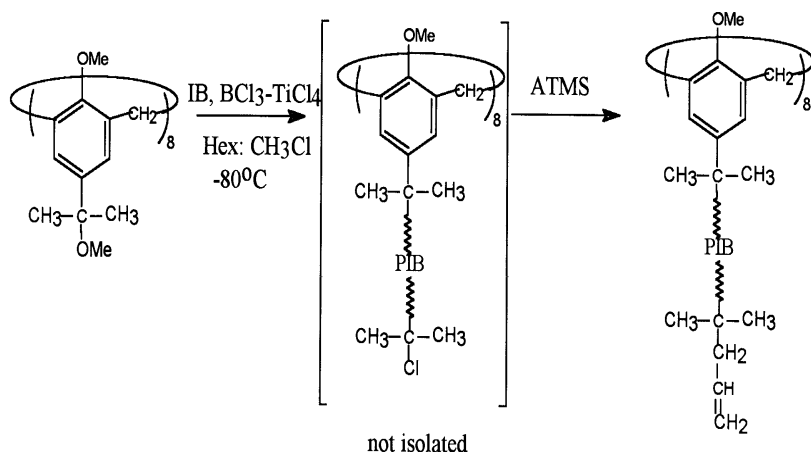
Scheme 2. Outline of the Synthesis of Allyl-Telechelic Octa-Arm Stars

Table. 1.   Molecular characteristics of two select allyl functionalized octa-arm PIB stars*.

| Initiator **1** mol x$10^{-5}$ | Star molecular weight, g/mol x $10^{-4}$ | | | | Arm molecular weight, *** g/mol x $10^{-3}$ | | End Functionality of Star**** | |
|---|---|---|---|---|---|---|---|---|
| | Observed** | | Calculated | $\overline{M}_w/\overline{M}_n$ | Obsd | Calculated | Obsd | Corrected$^{\dagger}$ |
| | $\overline{M}_n$(LLS) | $\overline{M}_w$(LLS) | $\overline{M}_n$(LLS) | | $\overline{M}_n$(LLS) | $\overline{M}_n$ | | |
| 3.52 | 5.36 | 5.77 | 4.94 | 1.08 | 6.7 | 6.2 | 9 | 8.1 |
| 3.19 | 9.79 | 11.1 | 8.78 | 1.13 | 12.2 | 11.0 | 8.9 | 8 |

* Synthesis conditions: For the conc. Of initiating sites the numbers in column 1 should be multiplied by 8 (i.e., by the number of potential initiating sites); [BCl$_3$] = 3 x (**1** x 8); [TiCl$_4$] = 8 x (**1** x 8); [DMA] = 2 x (1 x 8); [DtBP] = 1.03 x $10^2$ M; [ATMS] = 100 x (**1** x 8); -80°C; Stage I(60 min), Stage II (20 min); Stirring with ATMS 60 min; Volume of solvents = 25 mL; Conversions ~95%.

** Calculated by Astra 4.0; $\overline{M}_n$(LLS) data are meaningful since the molecular weight distribution are narrow

*** Calculated assuming arm number = 8

**** Calculated from $^1$H NMR spectroscopy data of virgin samples

$^{\dagger}$Assuming the presence of ~10% linear contaminant

## Conclusions

A core-first method was used to prepare *tert*-Cl and allyl end-functionalized octa-arm PIB stars. Characterization research indicated the expected structure and close to quantitative end-functionalization.
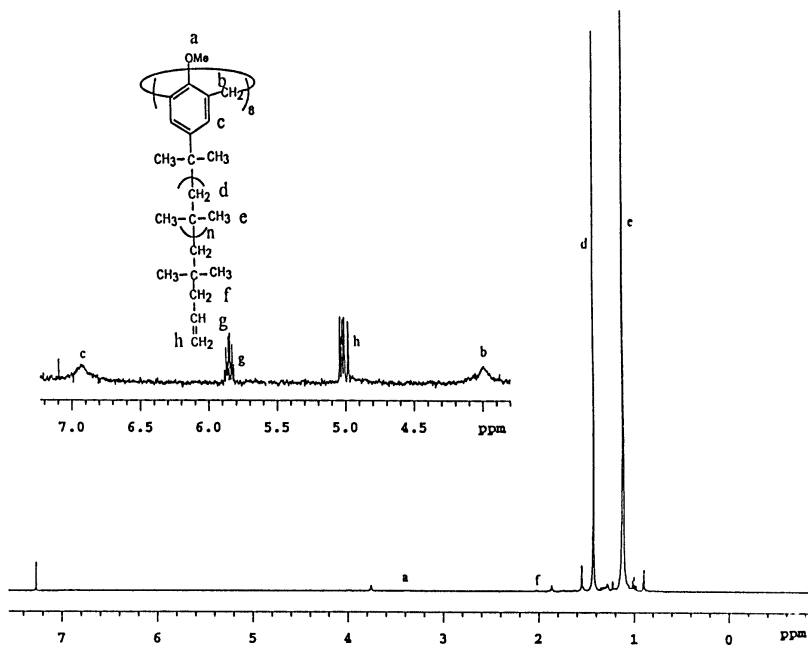
Fig. 4. $^1$H NMR (600 MHz) spectrum of allyl end-capped octa-arm PIB star ($\overline{M}_w = 11.0 \times 10^4$ g/mol) containing a calix[8]arene core.

## Acknowledgement

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