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Scale-up precision synthesis of octa-arm polyisobutylene stars[*]

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Summary

This paper concerns the scale-up precision synthesis of octa-arm polyisobutylene (PIB) stars. Specifically, we have optimized to the 100-200 g scale the preparation of star polymers consisting of eight PIB arms radiating from a calix[8]arene core. The synthesis strategy involved the use of a calix[8]arene fitted with eight p-$C(CH_3)_2OCH_3$ groups as the initiator in conjunction with mixed $BCl_3/TiCl_4$ coinitiators in hexanes/methyl chloride solvent systems at - 80 °C. Various possible side-reactions have been identified and means for their suppression/elimination were developed.

Introduction

In the course of our continued investigations on star-shaped polymers and copolymers [1-5], need arose to prepare 100 - 200 g quantities of multi-arm PIB stars with well-defined microarchitectures for property testing for various potential applications. Thus we decided to investigate the scale-up of earlier work that described the ~ 1 g scale synthesis of well-defined PIB stars consisting of a calix[8]arene core and eight PIB arms. During these investigations we have made several improvements which may be of use for future synthesis effort.

Experimental

Materials

Hexanes and CH_2Cl_2 were refluxed over calcium hydride (all from Fisher Scientific) under a nitrogen atmosphere for more than two days and then distilled. All the other chemicals used were from Aldrich and were used as received [1,6].

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[*] Part XXIV of the series "New Polyisobutylene Stars". For part XXIII see S. Asthana and J. P. Kennedy, *J. Polym. Sci.: Part A: Polym. Chem.*, in press.

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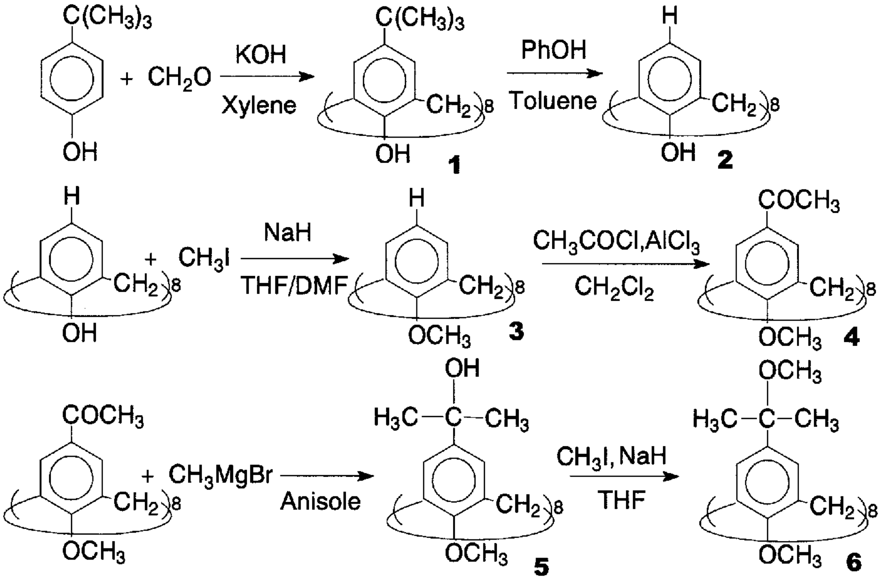
Isobutylene and methyl chloride (Mathesone® Gas Products) were dried by passing the gases through columns packed with barium oxide and molecular sieves, and condensed under a dry nitrogen atmosphere.

Initiator Synthesis

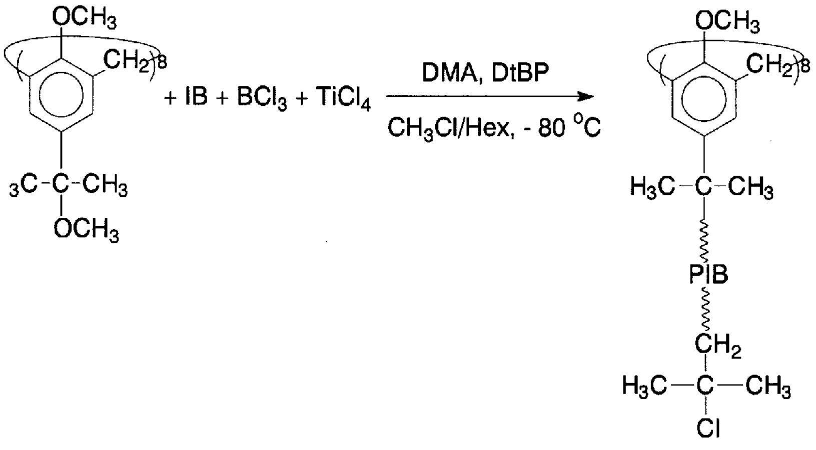
Scheme 1 outlines the steps leading to the octafunctional initiator. The ^{1}H NMR spectra of the intermediates (**1-5**) and that of the sought product **6** were identical to those described earlier [1,6].



Scheme 1. Synthetic route for the octafunctional calix[8]arene initiator (**6**)

The synthesis of octa-arm polyisobutylenes at the 100-200g scale

Scheme 2 summarizes the synthesis route:



Scheme 2. Synthesis of octa-arm star PIB

Following is a representative procedure for the preparation of an octa-arm PIB star with $M_{n,arm}$ = 20000 g/mol, that is, $M_{n,star}$ = 160,000 g/mol:

Polymerizations were carried out in 1000 mL, three neck flasks equipped with a mechanical stirrer. The octafunctional calix[8]arene-based initiator (**6**), 0.86 g ($5.63x10^{-4}$mol), was dissolved in 40 mL of CH_3Cl in a 75 mL culture tube and the initiator solution was poured into the reactor. In sequence, 160 mL of CH_3Cl, 25 mL of IB (0.32mol), 0.84 mL of dimethylacetamide (DMA, $9.02x10^{-3}$mol) and 1.01mL of di-*tert*-butylpyridine (D*t*BP, $4.51x10^{-3}$mol) were added to the charge, and the polymerization was induced by the addition of 13.50 mL of BCl_3 (1.0M solution in hexanes, $1.35x10^{-2}$mol BCl_3) at - 80 °C. After 60 minutes, 200 mL of hexanes and 50 mL of IB (0.64mol) were added and the polymerization was continued by the addition of 3.96 mL of $TiCl_4$ ($3.61x10^{-2}$mol). After 90 minutes, 50 mL of IB (0.64 mol), 300 mL of CH_3Cl/hexanes (50/50 v/v), 0.42 mL of DMA ($4.51x10^{-3}$mol) and 0.50mL of D*t*BP ($2.25x10^{-3}$mol), and 2 mL of $TiCl_4$ ($1.81x10^{-2}$mol) were added. After 150 minutes the polymerization was quenched by prechilled methanol. The solvents were evaporated and the polymer was redissolved in hexanes. The hexanes layer was washed with 5% HCl, water, and methanol. The hexanes were not fully evaporated (~ 18 wt% hexanes) to facilitate pouring the viscous product. Since IB conversion was essentially quantitative, this synthesis yielded ~ 90 g product.

The microstructure of the stars was established by GPC, LLS, and NMR spectroscopy as well as by core destruction [1,6].

Results and Discussion

Synthesis and characterization of the octafunctional initiator ***6***

The synthesis of **1-4** in Scheme 1 have been described [7,8]. During the preparation of **5**, to prevent dehydration, the product should be recovered by precipitation by the addition of excess of hexanes and not by solvent evaporation at higher temperatures and reduced pressures. Figure 1 shows the ^{1}H NMR spectrum of **6**. During the preparation of **6**, the organic layer has to be thoroughly extracted with ether to remove the initiator dissolved in the THF/water phase.

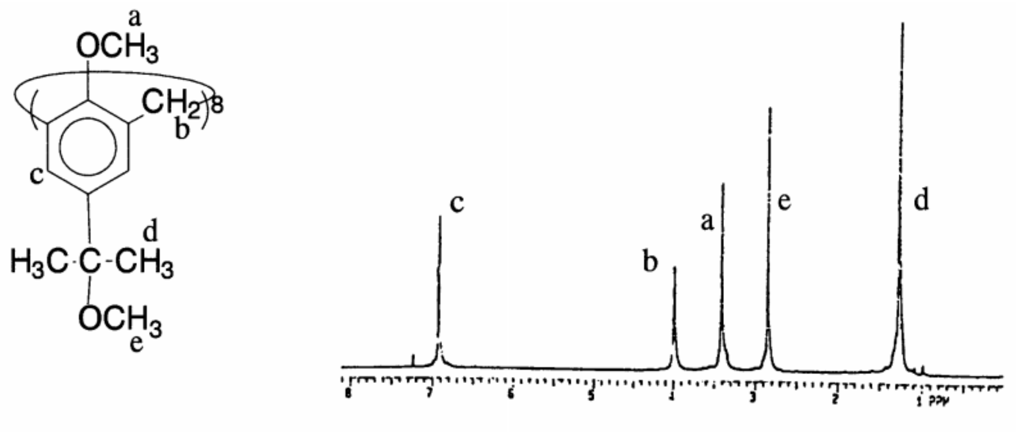


Figure 1. ^{1}H NMR spectrum of the calix[8]arene-based initiator **6**

Synthesis of octa-arm star polyisobutylene

We reconfirm that the precision synthesis of star PIBs by the calix[8]arene initiator requires the use of both BCl_3 and $TiCl_4$, in preference to the use of either of these Friedel-Crafts acids alone [1,6]. We found that polymerization by BCl_3 and $TiCl_4$ alone does not yield desired star product. The best result was obtained by the use of combinations of BCl_3 and $TiCl_4$. Table 1 shows representative results of IB polymerization at different BCl_3 and $TiCl_4$ concentrations. As shown in Table 1, BCl_3 alone did not yield sufficiently high molecular weight stars (most likely due to the relatively unstable BCl_4^- counteranion) [6,9], and $TiCl_4$ alone yielded multimodal molecular weight distributions by star-star coupling (see later). Since $TiCl_5^-$ is more stable than BCl_4^- proton elimination will occur preferentially with the former counterion [6,9]. The best result was obtained by the use of $[BCl_3]_0/[TiCl_4]_0$ ~ 0.4. During incremental monomer additions, additional amounts of solvents should be added to prevent the increase in solution viscosity. Also an additional amount of $TiCl_4$ should be added. Additional DMA and D*t*BP should also be added together with the incremental monomer additions. The optimum reagent concentration mole ratios used at Stage I (first $TiCl_4$ addition step) were [**6**]/8:$[BCl_3]_0$:$[TiCl_4]_0$:$[DMA]_0$: $[DtBP]_0$ = 1:3:8:2:1. The optimum ratios calculated at Stage III (final stage) were [**6**]/8:$[BCl_3]$:$[TiCl_4]$:[DMA]: [D*t*BP] = 1:3:12:3:2.

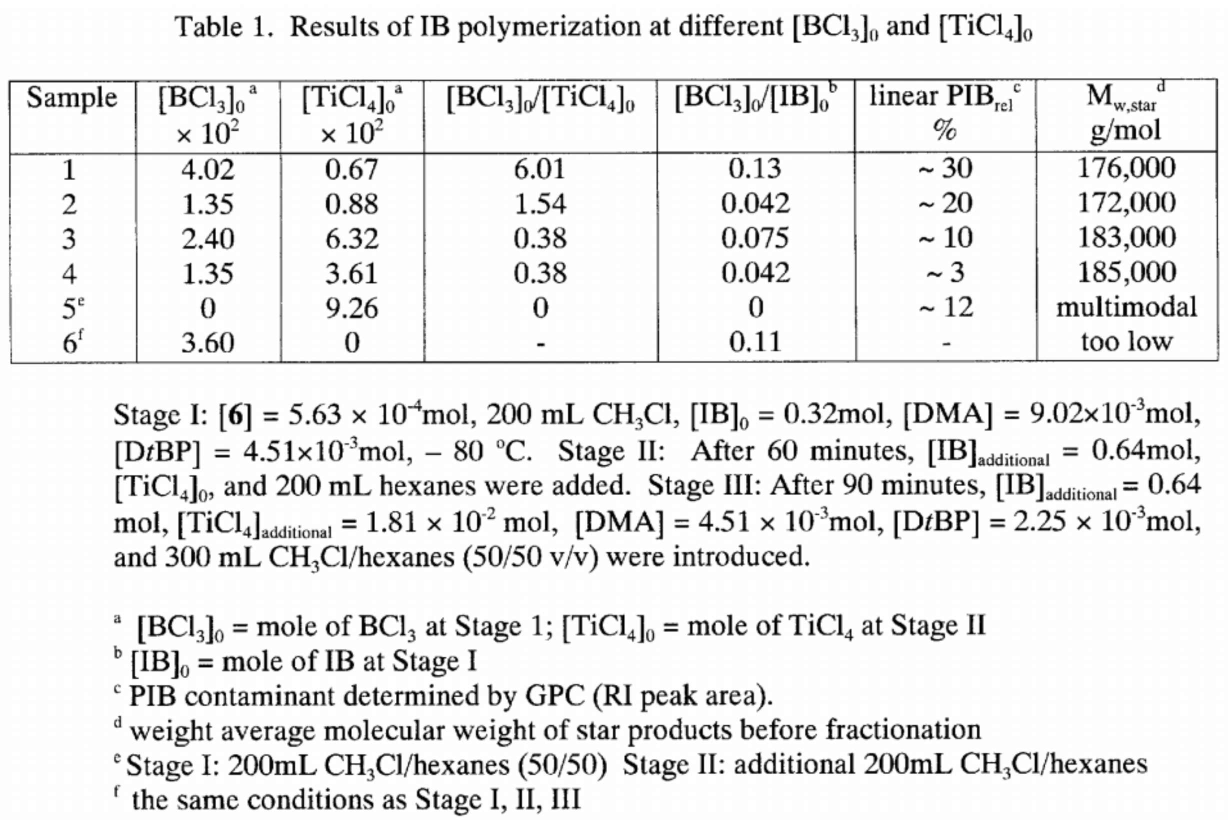


Table 1. Results of IB polymerization at different $[BCl_3]_0$ and $[TiCl_4]_0$

Sample	$[BCl_3]_0$[a] $\times 10^2$	$[TiCl_4]_0$[a] $\times 10^2$	$[BCl_3]_0/[TiCl_4]_0$	$[BCl_3]_0/[IB]_0$[b]	linear PIB_{rel}[c] %	$M_{w,star}$[d] g/mol
1	4.02	0.67	6.01	0.13	~ 30	176,000
2	1.35	0.88	1.54	0.042	~ 20	172,000
3	2.40	6.32	0.38	0.075	~ 10	183,000
4	1.35	3.61	0.38	0.042	~ 3	185,000
5[e]	0	9.26	0	0	~ 12	multimodal
6[f]	3.60	0	-	0.11	-	too low

Stage I: [**6**] = 5.63×10^{-4}mol, 200 mL CH_3Cl, $[IB]_0$ = 0.32mol, [DMA] = 9.02×10^{-3}mol, [D*t*BP] = 4.51×10^{-3}mol, – 80 °C. Stage II: After 60 minutes, $[IB]_{additional}$ = 0.64mol, $[TiCl_4]_0$, and 200 mL hexanes were added. Stage III: After 90 minutes, $[IB]_{additional}$ = 0.64 mol, $[TiCl_4]_{additional} = 1.81 \times 10^{-2}$ mol, [DMA] = 4.51×10^{-3}mol, [D*t*BP] = 2.25×10^{-3}mol, and 300 mL CH_3Cl/hexanes (50/50 v/v) were introduced.

[a] $[BCl_3]_0$ = mole of BCl_3 at Stage 1; $[TiCl_4]_0$ = mole of $TiCl_4$ at Stage II
[b] $[IB]_0$ = mole of IB at Stage I
[c] PIB contaminant determined by GPC (RI peak area).
[d] weight average molecular weight of star products before fractionation
[e] Stage I: 200mL CH_3Cl/hexanes (50/50) Stage II: additional 200mL CH_3Cl/hexanes
[f] the same conditions as Stage I, II, III

As shown in Figure 2, the main peak (~32 mL) is due to the sought star and the smaller peak (at ~35.5 mL) shows the presence of ~ 10 % linear PIB contaminant. This linear PIB contaminant is most likely due to initiation by protic impurities or chain transfer to IB or initiation by $Cl_2BCH_2C(CH_3)_2Cl$ formed by the possible chlorination of IB [1,6]. The first two side reactions may be reduced by the use of proton trap.

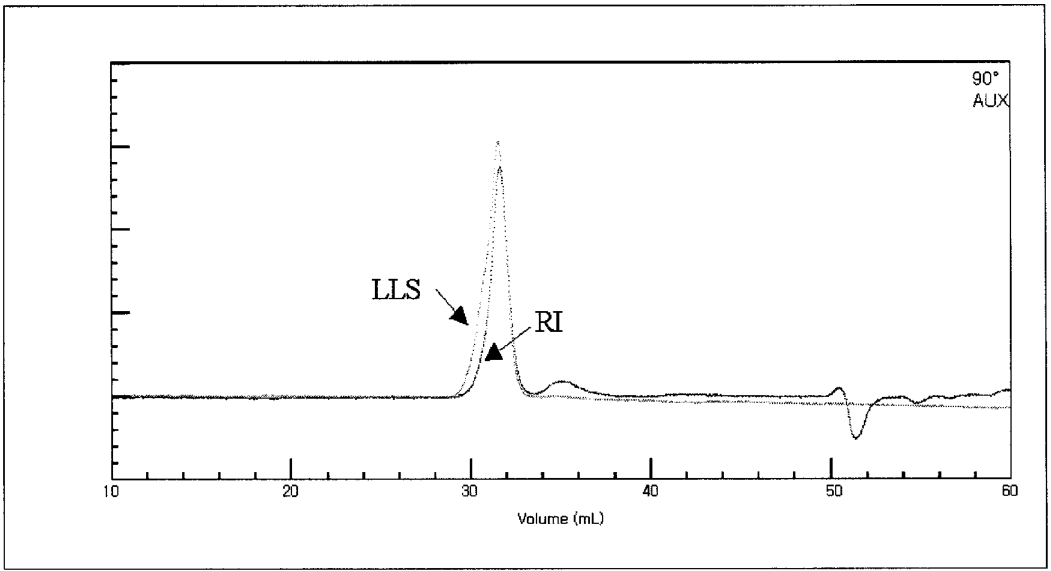


Figure 2. GPC traces (RI, LLS) of star PIB ($M_{w,star}$ = 183,000 and $M_{w,arm}$ = 23,000) (for experimental conditions, see sample no. 3 in Table 1)

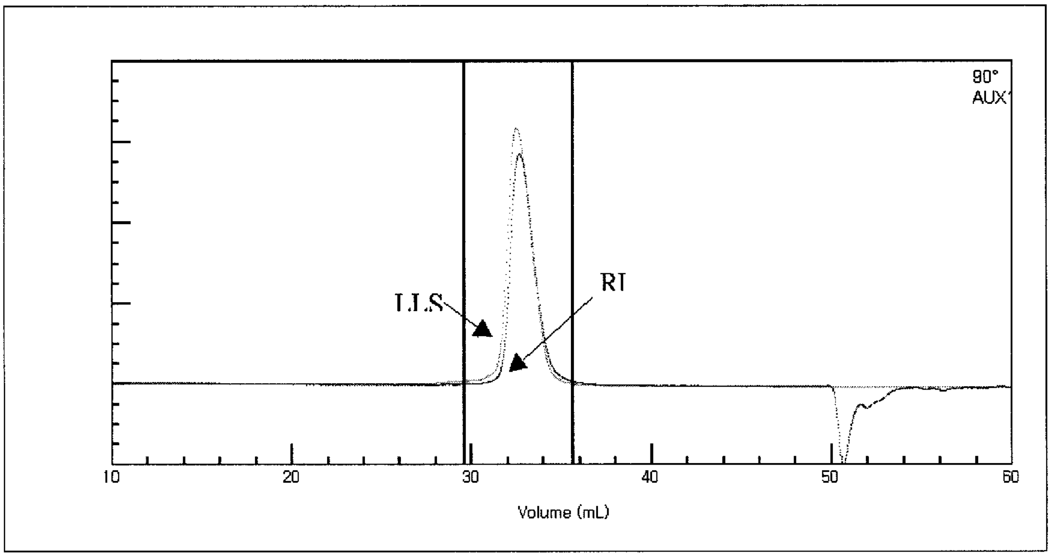


Figure 3. GPC traces (RI, LLS) of star PIB ($M_{w,star}$ = 185,000 and $M_{w,arm}$ = 23,000) (for experimental conditions, see sample no. 4 in Table 1).

Figure 3 shows a representative GPC chromatogram of a PIB star ($M_{w,star}$ = 185,000, $M_{w,arm}$ = 23,000) before fractionation. Stars were fractionated by dissolving them in hexanes and dropwise precipitating into acetone at room temperature. This procedure efficiently removed most low molecular weight PIB contaminants shown in Figure 2. As shown in Table 1 and Figure 3, the amount of PIB contaminant has decreased after using the lower $[BCl_3]_0/[IB]_0$ ratio, i.e., $[BCl_3]_0/[IB]_0 = 0.042$ (compare with the result in Figure 2, $[BCl_3]_0/[IB]_0 = 0.075$). Thus, the possibility of chloroboration of IB most likely decreases when the $[BCl_3]_0/[\text{monomer}]_0$ ratio is lowered during the first stage of IB polymerization.

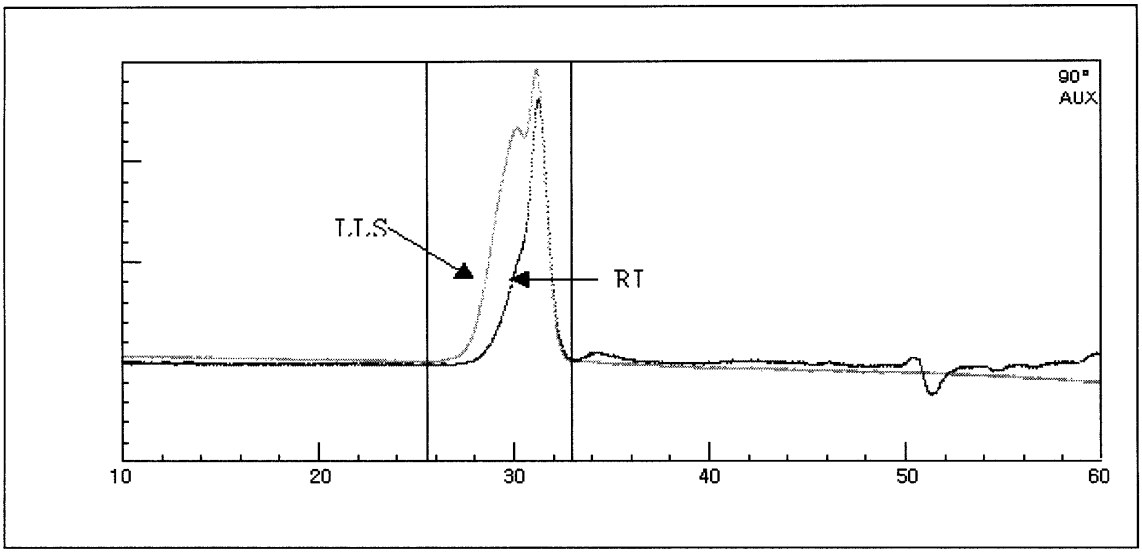
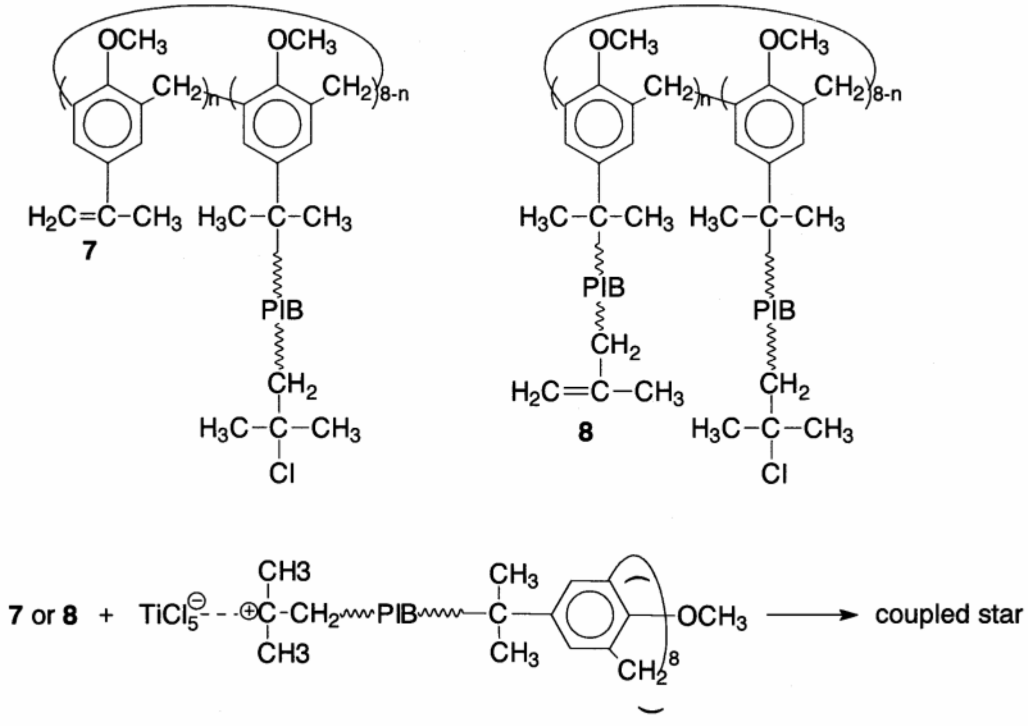


Figure 4. GPC traces (RI, LLS) of star PIB ($M_{w,star}$ = 307,000 and $M_{w,arm}$ = 38,000)

Star-star coupling

In several experiments the aim of which was the synthesis of well-defined high molecular weight star PIBs ($M_{w,arm}$ > 30,000 g/mol), we have obtained ill-defined multimodal products most likely due to star-star coupling mentioned above. As shown in Figure 4, the shoulder in the RI trace and the separate peak at ~30 mL in the LLS trace most likely indicate the formation of higher molecular weight star via star-star coupling. The mechanism of star-star coupling via reaction of the living cation and the isopropenyl group at the calixarene core (**7**, see Scheme 3) has been described in references [1,6]. The $PhC(CH_3)=CH_2$ groups can intermolecularly attack growing carbocations during the polymerization which leads to star-star coupling. Also during incremental monomer addition, deprotonation may occur at the propagating cation and give rise to $-CH_2C(CH_3)=CH_2$ (**8**, see Scheme 3) that will lead to coupling. To avoid this problem, incremental monomer additions were effected at less than ~100 % monomer conversion.

Also additional electron donor and proton trap were added during incremental monomer additions to maintain their initial concentrations. High dilution also helps to reduce the possibility of star-star coupling.



Scheme 3. Possible routes of star-star coupling

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