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An Alternative Multistep Linking Process for Making Asymmetric Star Polymers from Living Polymeric Arms

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Introduction

Star polymers comprise three or more arms extending outwardly from a nucleus.[4–22] The asymmetric star polymers, generally, contain arms of at least two different polymers, which may vary with chemical composition, structure, and/or molecular weight. A principal way of making asymmetric star polymers is to link various anionic polymeric arms mixed in the desired ratio with a linking agent which forms the nucleus of the star polymer. The problem, however, is that the product obtained contains a statistical distribution of all possible arm combinations. This problem, together with the incomplete linking resulting from the inability of the sterically hindered anion to undergo complete reaction with the multifunctional linking agent,[1–3] makes the structure control of asymmetric star polymers difficult.

Recently, it has been demonstrated that a well-defined, near-monodisperse, asymmetric star polymer can be produced by combining the arms with a multifunctional chlorosilane linking agent sequentially. Pennisi and Fetters[14] have devised a multiple-step linking approach to successfully synthesize three-arm polybutadiene and polystyrene star polymers where one of the arms possesses a molecular weight different from that of the remaining two identical arms. They also discovered that the addition of aprotic polar solvent or promoter would serve to decrease the extent of association of the styryllithium or alkenyllithium chain ends and result in complete linking of polymeric arms. Mays[18] employed the same approach to have prepared a mixed three-arm poly(isoprene-*graft*-styrene) copolymer. Iatrou and Hadjichristidis[21] have extended the approach to successfully synthesize a star polymer with three different arms, i.e., polyisopropene, polystyrene, and polybutadiene. The common approach they employed is, first, to link the odd arm with a large excess of linking agent to avoid the formation of double- or three-arm species, second, to remove the excess of linking agent by freeze-drying and vacuum pumping for a prolonged period of time, and third, to redissolve the single-arm species and link with the other arms. The characterization results of the resulting polymers indicate that their approach has led to well-defined, near-monodisperse, asymmetric star polymers.

The purpose of this work is to explore the feasibility of an alternative process without the need of adding a large excess of linking agent that would take several days to remove afterward. By taking advantage of the steric hindrance of the alkenyllithium chain ends and the linking enhancement of polar promoters, the proposed process starts with the linking of the major arms in the first step, leaving one empty site intact; the remaining odd arm is then linked to the empty site in the presence of a polar promoter. To study this linking process, gel permeation chromatography (GPC) has been heavily used.

Experimental Section

The asymmetric star polymer studied in this work was made of a total of four living polymeric arms (either homopolymer or block copolymer). Three of the four arms are identical, containing only polybutadiene, and the other arm is a block copolymer comprising one block of polystyrene and one block of polybutadiene. The target polybutadiene arms have a molecular weight of 22 000 each, and the target block copolymer arm has a polystyrene molecular weight and a polybutadiene molecular weight of 50 000 and 22 000, respectively. Both the polybutadiene arms and the block copolymer arm are living polymers containing a single lithium atom bonded to a terminal carbon atom and are readily made via anionic polymerization. They were made by polymerizing the butadiene and/or styrene monomers with an organo-alkali-metal compound, *sec*-butyllithium, in cyclohexane solvent at a temperature ranging from 25 to 75 °C in a closed dual-reactor system.

Formation of polybutadiene arms:

$$\mathrm{RLi} \xrightarrow{\text{butadiene}} \underset{(\mathrm{B^-Li^+})}{\mathrm{Rbbbb^-Li^+}} \tag{1}$$

Formation of block copolymer arms:

$$\mathrm{RLi} \xrightarrow{\text{styrene}} \mathrm{Rsss^-Li^+} \xrightarrow{\text{butadiene}} \underset{(\mathrm{SB^-Li^+})}{\mathrm{Rsssbbbb^-Li^+}} \tag{2}$$

where R = *sec*-butyl.

These two different kinds of polymeric arms were made separately and maintained separately until each was sequentially linked with the linking agent. Silicon tetrachloride having four functional groups, –Cl, which are reactive with lithium carbon bonds was used as the linking agent. Polybutadiene arms were first combined with the $SiCl_4$ at a temperature of 72 °C (except run 1 at 60 °C). The amount of polybutadiene arms used was sufficient to react with exactly three of the chlorine atoms attached to the $SiCl_4$. After the reaction was substantially complete, the reaction product was combined with the block copolymer arms at a temperature of 72 °C (except run 1 at 60 °C). A 10% excess of the block copolymer arms was used to force this second linking reaction to completion. The 10% excess means that a 10% excess of the block copolymer arms was used over and above that required to react with all of the remaining chlorine atoms on the initial silicon tetrachloride.

First linking step:

$$3\mathrm{B^-Li^+} + \mathrm{SiCl_4} \rightarrow \mathrm{ClSiB_3} + 3\mathrm{LiCl} \tag{3}$$

Second linking step:

$$\mathrm{SB^-Li^+} + \mathrm{ClSiB_3} \rightarrow \mathrm{(SB)SiB_3} + \mathrm{LiCl} \tag{4}$$

At the end, methanol was added to terminate the remaining living block copolymer arms. Molecular weight distributions of living polymeric arms and linked star polymers were analyzed by Waters gel permeation chromatography equipped with Waters M-486 absorbance (UV) and Waters 410 differential refractive index (RI) detectors. The GPC was operated using three DuPont PSM 1000 silica gel columns at a nominal flow rate of 0.5 mL/min with a sample concentration of 0.1% in THF solvent.

Results and Discussion

(1) Characteristics of the Polymeric Arms. The GPC chromatogram is used to determine the molecular weights of polymeric arms. Since the GPC instruments are calibrated using polystyrene standards of known narrow molecular weight, the molecular weight value of the polymer determined by GPC is "polystyrene equiva-

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Table 1. Characteristics of the Polymeric Arms by GPC

	$(MW)_{styrene}$ at peak	$(MW)_n$	$(MW)_w$	$(MW)_w/(MW)_n$	$(MW)_{true}$ at peak
polybutadiene	4.26×10^4	4.02×10^4	4.23×10^4	1.05	2.33×10^4
block copolymer	8.64×10^4	8.13×10^4	8.57×10^4	1.05	7.19×10^4

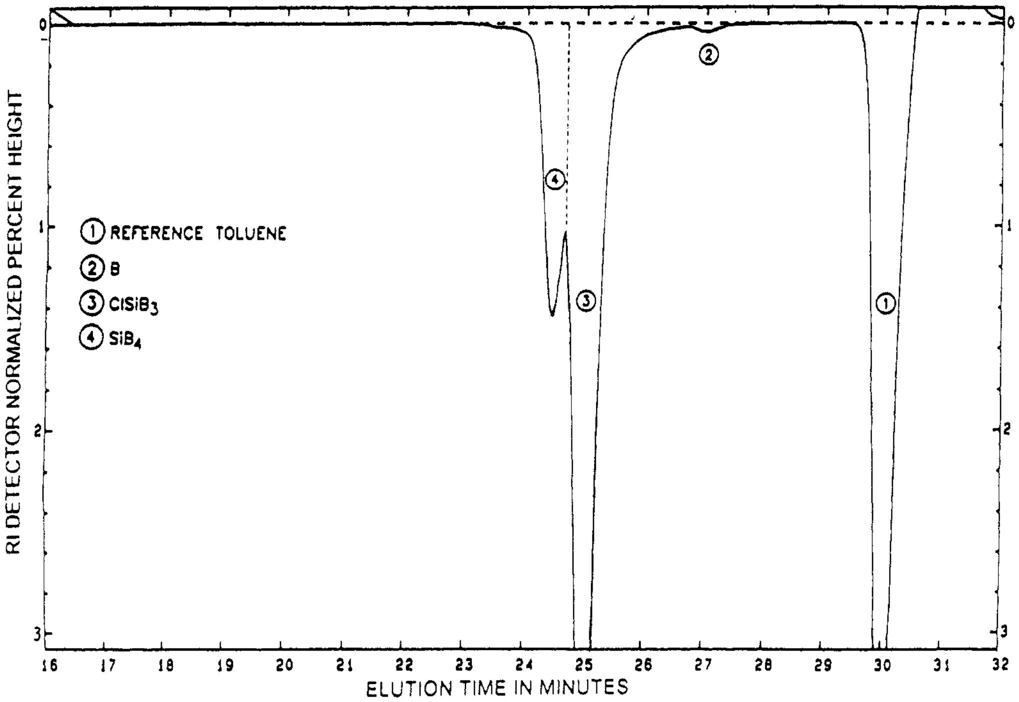

Figure 1. GPC analysis of MWD after the first linking step (with $SiCl_4$ undercharge).

lent" molecular weight. To translate this value to the true molecular weight of the polymer requires knowledge of the factor specific for that type of polymer. Previously, factors were developed for linear copolymers of styrene and butadiene.[23,24] As a result, the true molecular weights of the polybutadiene arms and the block copolymer arms can be determined via the following empirical correlation:

$$(MW)_{true} = F^x(MW)_{styrene}$$

where F is the factor for the butadiene portion of the polymer, and x is the weight fraction of the butadiene portion of the polymer. The value of the term F^x goes to the value F at pure polybutadiene and to 1 at pure polystyrene. The value of F was previously determined as 0.548–0.571.[23,24] Using a value of 0.548 in this work, the true molecular weights of polybutadiene arms and block copolymer arms were calculated as 2.33×10^4 and 7.19×10^4, respectively. The characteristics of the polymeric arms are listed in Table 1.

(2) Molecular Weight Distribution of the Star Polymer. Equations 3 and 4 represent an ideal two-step linking method for the synthesis of our target asymmetric star polymers. During the first linking step, every 3 mol of B^-Li^+ are linked with $SiCl_4$ to form 1 mol of $ClSiB_3$. This $ClSiB_3$ is then linked during the second linking step with SB^-Li^+ to constitute the final molecules, $(SB)SiB_3$. However, during our synthesis there existed inevitably small amounts of other species such as Cl_3SiB, Cl_2SiB_2, and SiB_4 after the first linking reaction. These species except the inert SiB_4 would participate in the second linking reaction, generating high molecular weight molecules, namely, $(SB)_2SiB_2$ and $(SB)_3SiB$.

In order to minimize the formation of species other than $(SB)SiB_3$, controlling the amount of $SiCl_4$ charge is extemely important. Any undercharge of $SiCl_4$ would provide an insufficient number of linking sites, leading to the formation of SiB_4, and any overcharge of $SiCl_4$ would generate too many linking sites, resulting in an increased amount of Cl_3SiB and Cl_2SiB_2. The molecular weight distribution of the resulting polymers caused by undercharge and overcharge of $SiCl_4$ can be seen in Figures 1 and 2 and Figures 3 and 4 respectively. In comparison, a good control of $SiCl_4$ charge has led to a molecular weight distribution such as that shown in Figures 5 and 6.

(3) Kinetics of the Second Linking Step. During and after the linking of the block copolymer arms the reaction product was sampled at 10 min, 60 min, and 24 h for GPC analysis to examine the linking efficiency. Within experimental error and instrument accuracy, the linking efficiencies (LE) have been calculated from the peak areas of the GPC chromatogram based on both UV and RI curves in the following way:

$$LE = \frac{\text{peak area of } (SB)SiB_3}{\text{peak areas of all SB-containing species}} \qquad (5)$$

Since the UV detector detects styrene only, the area of each molecule peak in the UV curve reflects the amount of styrene contained in that molecule. As a result, the linking efficiency calculated from the UV curve using eq 5 has a meaning of the percent of SB arms that has been linked to form the $(SB)SiB_3$ star polymer. On the other hand, the RI detector detects all species; therefore, the linking efficiency calculated from the RI curve using eq 5 represents the mass ratio of $(SB)SiB_3$ to all SB-containing species. It is important to note that the use of the RI curve suffers from the drawback that the voltage signal of the detector is critically dependent upon dn/dc, i.e., the

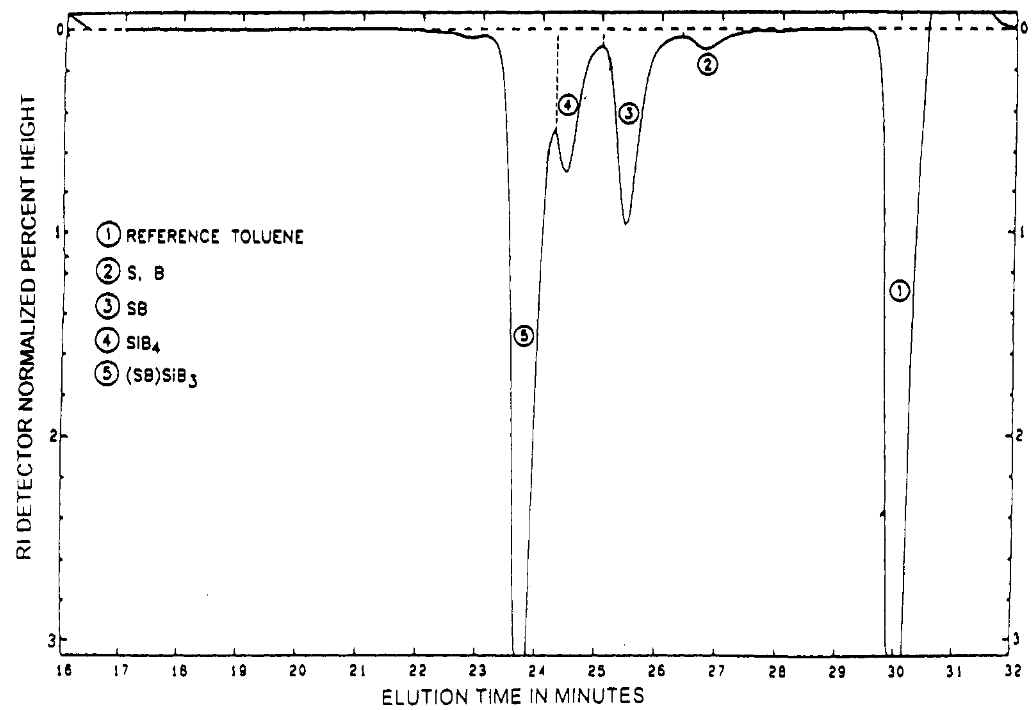

Figure 2. GPC analysis of MWD after the second linking step (with $SiCl_4$ undercharge).

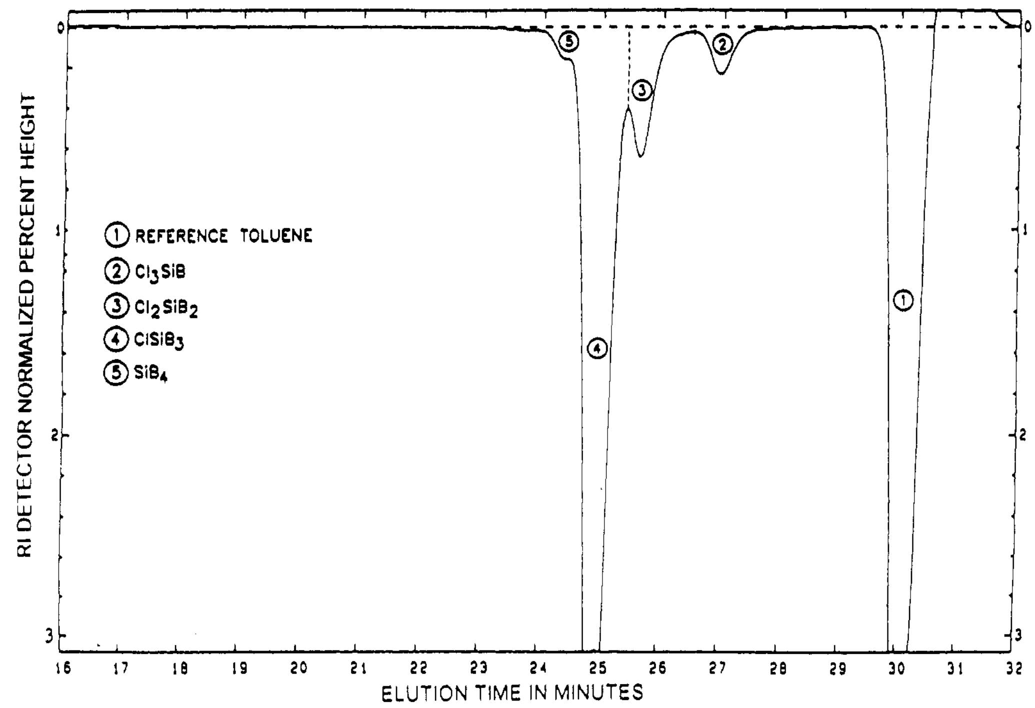

Figure 3. GPC analysis of MWD after the first linking step (with $SiCl_4$ overcharge).

refractive index increment with molecular concentration.[25] For copolymers such as the star polymer studied in this work, this quantity can vary with molecular weight and be different at each GPC eluant fraction. As a result, linearly relating the voltage signal to the concentration of molecular species may contain significant error. Therefore, the linking efficiencies calculated from the RI curve should only be viewed as qualitative. Since the maximum stoichiometric linking efficiency achievable is 91% by UV and 95% by RI (due to a 10% excess of block copolymer arms added during the second step linking reaction) and the maximal achieved efficiency varies as a result of their sensitivity to the metering inaccuracy, the normalized linking efficienies, defined as the linking efficiencies divided by their respective maximal achieved values, were used to illustrate the second step linking kinetics. The normalized linking efficiencies for the first three runs were determined at the three times tested, as shown in Table 2. The linking kinetics is slow, and high linking efficiency is hard to achieve without lengthy linking time. Although elevating the linking temperature from 60 to 72 °C did cause some rate improvement, further increasing the linking temperature was not attempted because higher temperature would cause significant thermal deactivation of the living polymeric arms.

Runs 4 and 5 were conducted in the same manner as runs 1–3 except that 50 ppm ethylene glycol diethyl ether was added as the linking promoter prior to the inception

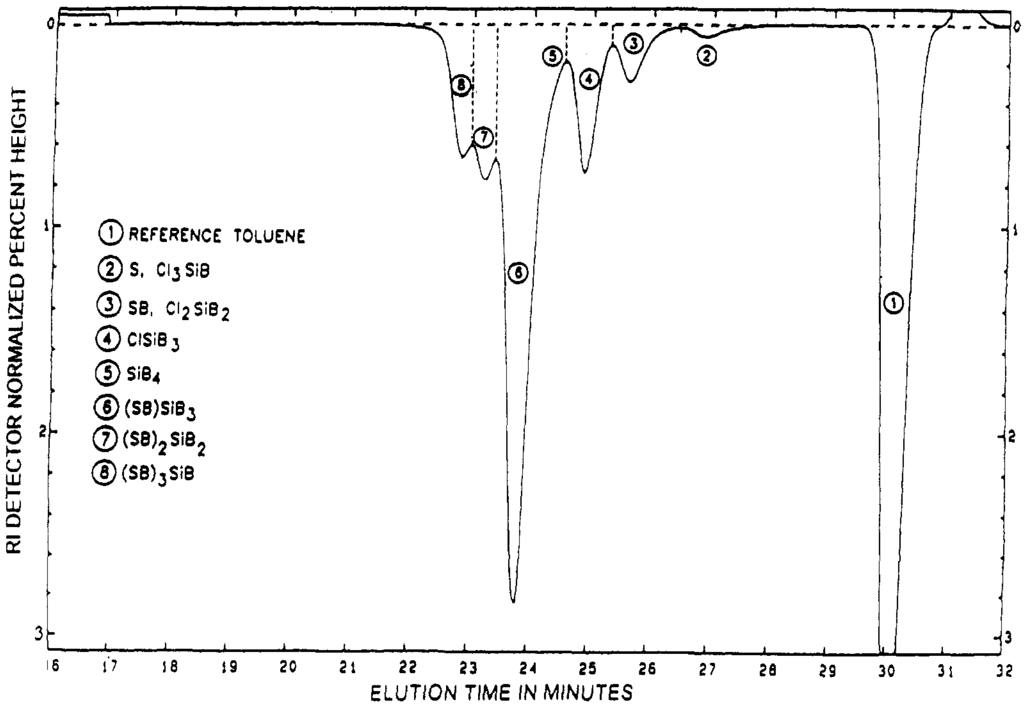

Figure 4. GPC analysis of MWD after the second linking step (with $SiCl_4$ overcharge).

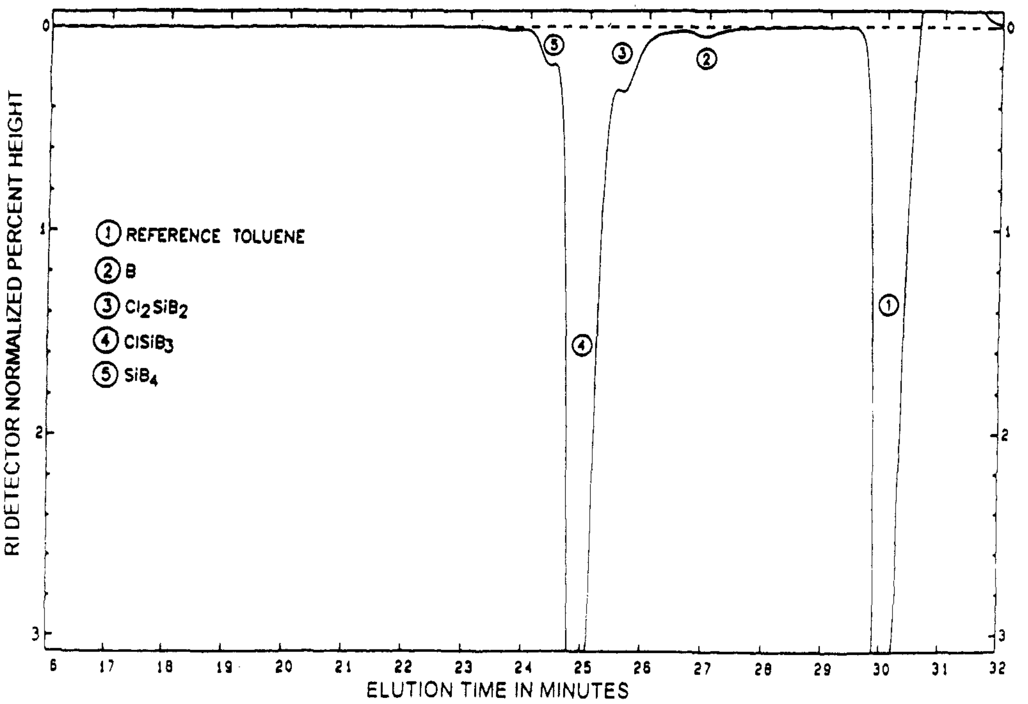

Figure 5. GPC analysis of MWD after the first linking step (with exact $SiCl_4$ charge).

of the second linking step. The normalized linking efficiencies were again determined at 10 min, 60 min, and 24 h.

In runs 6 and 7, the asymmetric star polymer was prepared using 200 ppm o-dimethoxybenzene (ODMB) as the linking promoter. Otherwise, the experiment was conducted under conditions identical to those experiments using ethylene glycol diethyl ether. The reaction product was again sampled at 10 min, 60 min, and 24 h to determine the linking efficiency at each of these times.

Run 8 was conducted in the same manner as runs 6 and 7 except that 100 ppm ODMB was substituted for the 200 ppm ODMB.

The data of second step linking kinetics for runs 4–8 are summarized in Table 3. Since runs 1–3 were conducted without adding any linking promoter, they provide a basis of comparison between runs completed with polar compound and runs completed without polar compound. As will be apparent from Table 3, the linking efficiency is significantly better at 10 min when an ether (both ethylene glycol diethyl ether and ODMB are polar ethers) is used, and this is true when a concentration as low as 50 ppm ethylene glycol diethyl ether is used. The results get closer with and without an ether at 60 min, and data from run 8 suggest an optimum concentration, at least, with ODMB of about 100 ppm. In this regard, it is believed that both concentration and activity effect the result with any given ether and it whould be possible to find an optimum concentration of any ether.

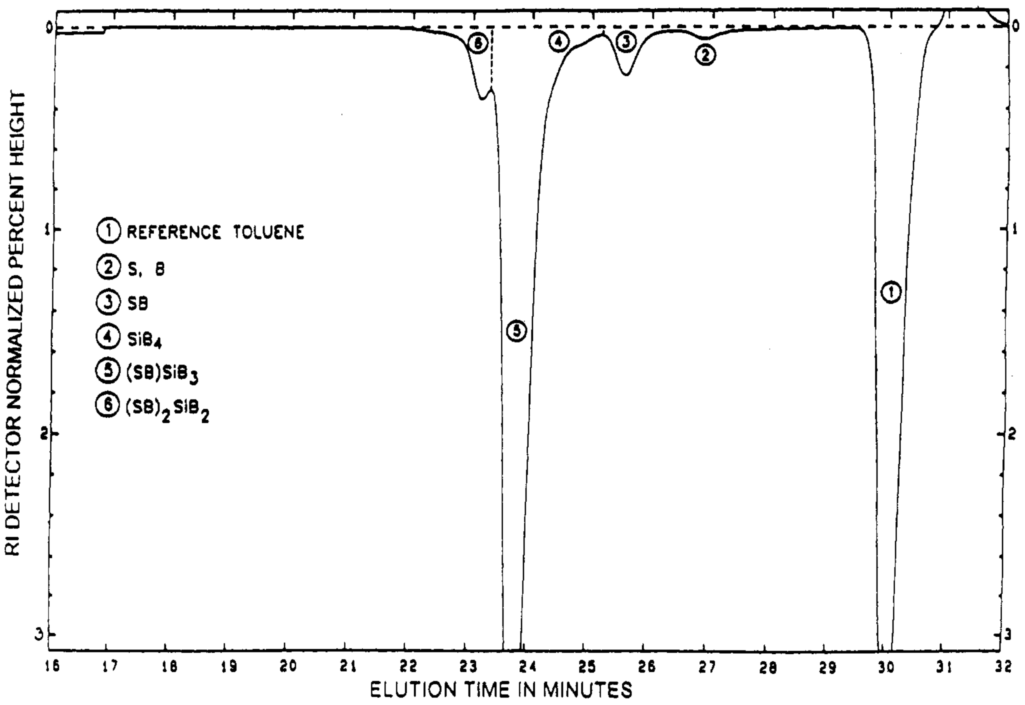

Figure 6. GPC analysis of MWD after the second linking step (with exact SiCl$_4$ charge).

Table 2. Kinetics of the Second Linking Step for Runs without Polar Compound

	normalized linking efficiency, %					
	from UV detector			from RI detector		
run no.	10 min	60 min	24 h	10 min	60 min	24 h
1 (60 °C)	29.8	88.3	100	40.7	91.7	100
2 (72 °C)	54.4	96.6	100	65.6	97.8	100
3 (72 °C)	34.5	95.8	100	43.7	97.4	100

Table 3. Kinetics of the Second Linking Step for Runs with Polar Compound

	normalized linking efficiency, %					
	from UV detector			from RI detector		
run no.	10 min	60 min	24 h	10 min	60 min	24 h
4 (72 °C)	94.2	96.5	100	96.0	97.6	100
5 (72 °C)	85.7	99.8	100	88.9	94.8	100
6 (72 °C)	99.7	99.9	100	99.7	99.9	100
7 (72 °C)	98.6	99.4	100	99.0	99.7	100
8 (72 °C)	99.7	100	100	100	100	100

Concluding Remarks

An alternative linking process of making asymmetric star polymers where one of the arms differs in molecular weight and composition from the remaining arms has been demonstrated. This process requires (1) the major arms constituting the asymmetric star polymer be linked first with the linking agent under conditions that one linking site is left intact due to steric hindrance and (2) a suitable polar compound be added immediately prior to the time the other arm is linked to the last site of the linking agent. The multistep linking process enables us to make a well-defind, asymmetric star polymer with a desired arm ratio, and the addition of polar promoters such as *o*-dimethoxybenzene and ethylene glycol diethyl ether allows the linking of the last arm to complete in a relatively short period of time.

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