Synthesis and Characterization of Polyisoprene/Polybutadiene A_2B_2 Star Copolymers

Jürgen Allgaier and Ronald N. Young*

Department of Chemistry, University of Sheffield, Sheffield S3 7HF, Great Britain

Vasilis Efstratiadis and Nikos Hadjichristidis

Department of Chemistry, University of Athens, Panepistimiopolis, Zografou, 15771 Athens, Greece

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ABSTRACT: Two routes for the synthesis of star block copolymers having exactly two arms of polyisoprene (PI) and two of polybutadiene (PB) are described. The first route starts by condensing one molecule of silicon tetrachloride with two of poly(isoprenyl)lithium which has been end-capped by a few units of styrene. The second route starts by linking two poly(isoprenyllithium) chains with one molecule of silicon tetrachloride at a suitably reduced temperature. Both routes are completed by reaction of the two-armed intermediate $(PI)_2SiCl_2$ with an excess of poly(butadienyllithium). The resulting $(PI)_2Si(PB)_2$ star polymer was purified by fractionation. The reaction steps were monitored by size exclusion chromatography and the products characterized by low-angle laser light scattering, osmometry, and NMR.

Introduction

The most convenient way to synthesize star polymers with a defined number of arms is by the linkage of reactive chain ends, synthesized via anionic polymerization, using multifunctional chlorosilane compounds.[1−15] This method allows not only the production of star homopolymers but also of stars having arms differing in composition.[16−19] For example, to realize the synthesis of an A_2B_2 star using $SiCl_4$ as the linking agent, a means has to be found whereby two, and only two, of the chlorine atoms can be reacted with two living polymer chains of composition A. Completion of the synthesis of the star by subsequent reaction with two living chains of B is expected to be straightforward. Indeed, A_2B_2 star copolymers having two polystyrene arms (PS) together with either two of PI or PB were successfully synthesized in this manner.[19] Provided a hydrocarbon solvent is employed, the reaction of the living PS chain end with $SiCl_4$ virtually stops after the addition of two PS chains—presumably as a consequence of steric hindrance to the entry of a third PS chain. Poly(styryllithium) is present in hydrocarbon solvents virtually entirely as dimers, together with a small proportion of higher aggregates.[20−23]

Preliminary studies showed that, in contrast, the reaction of the sterically less hindered polyisoprenyl and polybutadienyl chain ends with $SiCl_4$ does not stop after the linkage of two polymer chains. For this reason an A_2B_2 star block copolymer containing two PI and two PB chains cannot be obtained by conventional consecutive addition of the two living polymers. The present work was undertaken to establish a route which would permit the substitution of uniquely two of the chlorine atoms in $SiCl_4$ as the necessary starting point for the synthesis of perfect A_2B_2 stars.

Experimental Section

Cyclohexane (Aldrich) and *n*-heptane (Merck) were distilled from Na/K alloy and then from *n*-butyl lithium. Benzene was purified by sequential distillation from CaH_2, *n*-butyllithium, and poly(styryllithium). Isoprene (Fluka) was purified by treatment with dibutylmagnesium for 12 h, then distilled onto *n*-butyllithium, and allowed to stand for 30 min at −20 °C immediately before use. Butadiene (Aldrich) was purified by distillation onto a sodium mirror. After repeating this procedure twice, it was distilled onto *n*-butyllithium and allowed to stand for 30 min at −20 °C before being transferred into ampules. Tetrahydrofuran (THF) was purified by sequential distillation from calcium hydride, a sodium mirror, the purple benzophenone/sodium adduct, and finally (1,1-diphenylhexyl)-lithium. Triethylamine (Fluka) was purified by treatment with *n*-butyllithium and distilled into ampules. 1,1-Diphenylethylene (DPE) was purified by vacuum titration of the impurities with a 15% solution of *n*-butyllithium in *n*-hexane.

sec-Butyllithium (Aldrich) was distilled under high-vacuum conditions, then diluted with cyclohexane and subdivided into ampules. The concentration was determined by hydrolyzing an aliquot with water and titrating the LiOH formed with standard hydrochloric acid. $SiCl_4$ (Aldrich) was purified by distillation on the vacuum line: the first third of the distillate was discarded but the next third was collected, diluted with cyclohexane or benzene, and transferred into ampules. The concentration was determined by hydrolyzing an aliquot with water and titrating the HCl formed with standard sodium hydroxide solution.

All manipulations were performed under high vacuum in glass reactors, provided with break seals for the addition of reagents. *sec*-Butyllithium was used as the initiator for all polymerizations. Greaseless stopcocks were used in some cases to permit the removal of samples from the reactor. The polymers were isolated and fractionated, using toluene as solvent and methanol as nonsolvent. The microstructures and the compositions were determined by ^1H NMR spectroscopy in $CDCl_3$ at 30 °C using a 300 MHz Varian spectrometer.

Some of the SEC experiments were carried out at 30 °C, using a Waters Model 510 pump and a Waters Model 401 differential refractometer. Four μ-Styragel columns with a continuous porosity range from 10^6 to 10^3 Å were used (SEC a). The other SEC experiments were performed using a Waters Model 6000 pump and a Knauer differential refractometer together with three 60 cm Phenomenex 5 μm mixed gel columns (SEC b). Polystyrene standards were used for calibration and Polymer Laboratories LogiCal software was used for analysis; corrections were made to allow for star architecture and composition. In all experiments the eluant was THF at a flow rate of 1 mL/min.

Weight-average molecular weights (M_w) were measured by low-angle laser light scattering (LALLS) at 25 °C with a Chromatix KMX-6 LALLS photometer. This instrument was equipped with a helium−neon laser operating at a wavelength

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of 633 nm. The solvent was purified THF, redistilled from sodium immediately prior to use. The refractive index increments d*n*/d*c* in THF at 25 °C were measured with a Chromatix KMX-16 differential refractometer, operating at 633 nm and calibrated with aqueous NaCl solutions. For all star polymers d*n*/d*c* was found to be 0.134. The M_w values were obtained from the corresponding $(Kc/\Delta R\vartheta)^{1/2}$ vs c plots, where K is a combination of known optical constants, c the concentration, and $\Delta R\vartheta$ the excess Rayleigh ratio.

Number-average molecular weights (M_n) for the stars were determined at 35 °C with a Wescan Model 231 membrane osmometer. The solvent was toluene which had been distilled from CaH_2. M_n values were obtained from the corresponding $(\pi/c)^{1/2}$ vs c plots, where π is the osmotic pressure. The M_n values for the arms were determined using a Jupiter 833 vapor pressure osmometer.

The sample compositions were determined by ^1H NMR in $CDCl_3$ at 30 °C, using a 300 MHz Varian spectrometer.

Results and Discussion

Hypothetically, the synthesis of A_2B_2 heteroarm star copolymers containing PI and PB arms could be accomplished directly by the sequence

$$2PILi + SiCl_4 \rightarrow (PI)_2SiCl_2 + 2LiCl$$

$$(PI)_2SiCl_2 + \text{excess } PBLi \rightarrow (PI)_2(PB)_2Si + 2LiCl$$

However, both PILi and PBLi living chain ends are very reactive toward $SiCl_4$ and, accordingly, limiting the coupling to only two living chain ends with a single molecule of $SiCl_4$ in the first reaction step presents serious difficulties. Some three-armed star $(PI)_3SiCl$ is also formed because of the small difference in reactivity between the substitution of the second and the third chlorine atoms. One potential means of preventing substitution of the third chlorine atom is to cap the living chain ends with a few units of a bulky monomer. As an alternative, a means may be sought to lower the overall reactivity of the living polymer toward $SiCl_4$ in the expectation that the differences in the rates of the successive linking steps may be enhanced, thereby facilitating selectivity. A potential means of achieving this end is to lower the reaction temperature. Both methods have been investigated.

End-Capping Protocol. Initial experiments were conducted in which poly(isoprenyllithium) in benzene solution was end-capped with 1,1-diphenylethylene (DPE)—a molecule incapable of polymerization. Unfortunately, although this adduct reacted quite readily with $SiCl_4$ to replace one atom of chlorine, the replacement of a second atom was extremely slow. After 2 weeks only 20% of the $(PI)SiCl_3$ had been converted to $(PI)_2SiCl_2$. At this point a small quantity of THF was added and, as a result, the conversion reached 50% after a further week. It was clear that the steric effect of capping with DPE was too severe.

Since it is known that only two molecules of poly(styryllithium) will react at all rapidly with one of $SiCl_4$ in benzene solution, capping poly(isoprenyllithium) with styrene would seem to provide an obvious protocol. However, the rate of this crossover reaction is comparable to the subsequent rate of propagation of the residual styrene. To ensure that all chains are capped—but with only a few units of styrene—it was necessary to cap in the presence of a trace of THF. Because THF also catalyzes the reaction of the active chain ends with $SiCl_4$, the amount of it must be kept minimal. In practice, a benzene solution of styrene was added to the poly(isoprenyllithium) in the ratio [styrene]:[Li] of 3:1 followed by THF such that [THF]:[Li] was about 20:1. The subsequent linking with $SiCl_4$ was conducted in two stages. One equivalent of capped poly(isoprenyllithium) was added to one of $SiCl_4$ in a single step. Therafter, the second equivalent was titrated into the reactor in successive aliquots, with the progress of reaction being monitored by removing samples from the reactor and analyzing them by SEC. In this manner, it proved possible to prepare $(PI)_2SiCl_2$ free from three-armed contaminant, as is shown by the SEC trace (Figure 1). The synthesis of the Is_2Bd_2 star was completed by the introduction of poly(butadienyllithium) in small excess (ca. 10%) over that required for stoichiometry and the reaction mixture was allowed to stand for 2 weeks. Figure 2 shows the SEC traces of the polyisoprene and polybutadiene arms, the intermediate $(PI)_2Cl_2$, the final reaction mixture, and the pure star obtained by fractionation. The molecular weight data collected in Table 1 provide convincing evidence that this synthetic procedure is highly effective for the preparation of these A_2B_2 heteroarmed star copolymers.

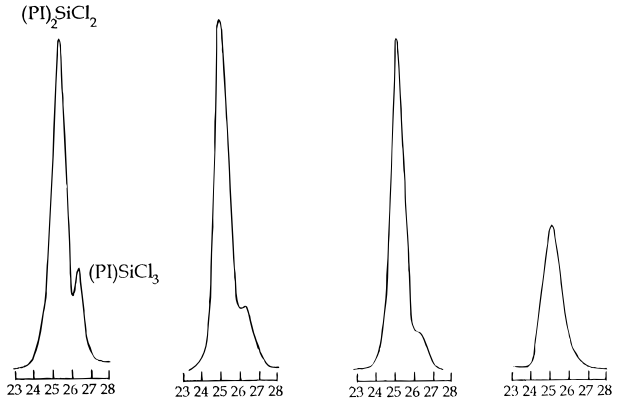

Figure 1. SEC traces taken during the titration of styrene-capped poly(isoprenyllithium) with $SiCl_4$.

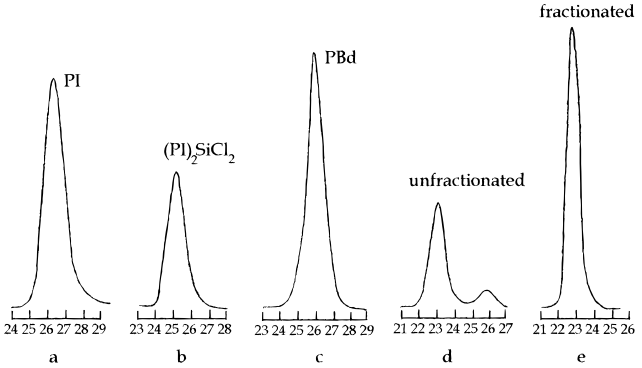

Figure 2. SEC traces of (a) styrene-capped poly(isoprenyllithium), (b) the coupled product $(PI)_2SiCl_2$ formed on titrating $SiCl_4$, (c) the PB sample recovered from the PBLi used to attach the third and fourth arms, and the $(PI)_2Si(PB)_2$ star before (d) and after (e) fractionation.

Low-Temperature Protocol. This method does not involve the end-capping of the living chain ends. Instead, the reactivity of the system is reduced by lowering the reaction temperature during the linking of the first kind of polymer chain. It is to be expected that as a consequence of mounting steric hindrance, the activation energies for the replacement of the four chlorine atoms of $SiCl_4$ will increase at each successive step. In accordance with the Arrhenius equation, the *relative* rates of reaction will become more different when the reaction temperatue is lowered. Whether or not this can be exploited as a *practicable* means of creating

Table 1. Molecular Weights and Dispersities of Stars Formed by Capping[a]

	PI arm		PB arm		star			
sample	M_n (VPO)	D (SEC a)	M_n (VPO)	D (SEC a)	M_n (MO)	M_w (LALLS)	D (MO/LALLS)	D (SEC a)
IB5	4800	1.05	7300	1.04	24200	25200	1.04	1.04
IB8	8600	1.04	7300	1.04	32500	34400	1.06	1.05
IB15	14900	1.04	6600	1.03	42300	44000	1.04	1.03

[a] VPO = vapor phase osmometry, MO = membrane osmometry, LALLS = low-angle laser light scattering.

Table 2. Molecular Weights and Dispersities of Stars Formed by Temperature Control[a]

	PI arm		PB arm		$(PI)_2SiCl_2$		star			
sample	M_n (SEC b)	D (SEC b)	M_n (SEC b)	D (SEC a)	M_n (SEC b)	D (SEC b)	M_n (MO)	M_w (LALLS)	M_n (SEC a)	D (SEC a)
I_5B_7	5000	1.04	6900	1.03	10100	1.05	22600	25300	22700	1.07
I_8B_7	7800	1.03	6600	1.03	16200	1.03	28600	28900	27600	1.05
$I_{15}B_7$	14400	1.03	6600	1.03	31000	1.03	41500	42400	40200	1.03

[a] VPO = vapor phase osmometry, MO = membrane osmometry, LALLS = low-angle laser light scattering.

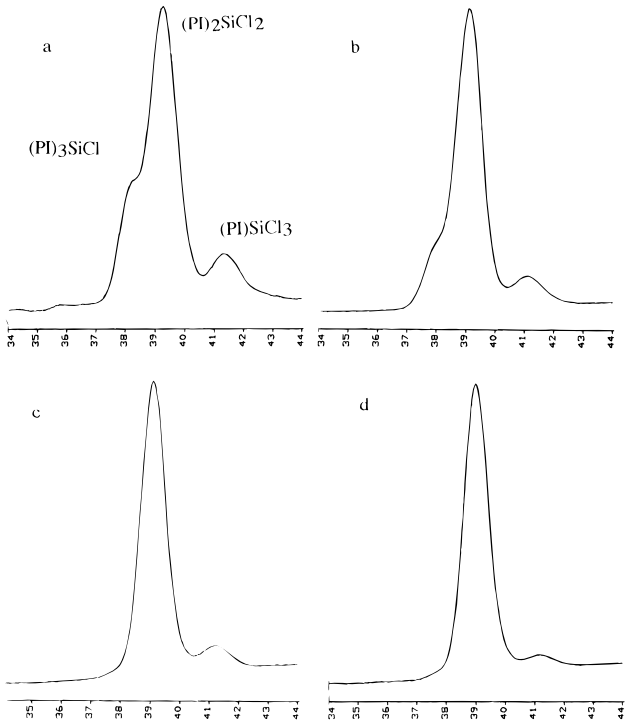

Figure 3. SEC traces for the reaction of poly(isoprenyllithium) with $SiCl_4$ conducted at different temperatures: (a) at 20 °C; (b) at −20 °C; (c) at −40 °C; (d) at −40 °C for 3 days followed by a further day at −30 °C.

selectivity of the number of arms introduced must depend upon the differences in activation energies.

In order to avoid freezing, *n*-heptane was used as the solvent. The first stage of linking involved adding a solution of $SiCl_4$ to one of PILi having a molecular weight of about 8000 at the appropriate temperature. The molar ratio of PILi to $SiCl_4$ employed was 2.03. This slight excess of polymer over the stoichiometric requirement was chosen as a safeguard against the possibility that the $SiCl_4$ might contain traces of reactive impurities. The progress of the linking process was monitored by removing samples from the reactor. Care was taken to ensure that these samples were not warmed above the reactor temperature before being quenched with methanol. The SEC analysis of samples, taken after 3 days, is shown in Figure 3. At a reaction temperature of +20 °C (Figure 3a) the two-armed product was the majority species formed. However, the shoulder at higher molecular weight indicates that a considerable amount of three-armed star $(PI)_3SiCl$ was also formed. As a consequence of the ratio of PILi to $SiCl_4$ being nearly exactly 2, the same amount of one-armed product ($PISiCl_3$) as three-armed star should be formed when reaction has eventually gone to completion. It is not believed that any of the $PISiCl_3$ peak should be attributed to PILi "killed" by adventitious impurities present in the reaction mixture. When the linking reaction was conducted at −20 °C (Figure 3b), the amounts of three-armed star and of one-armed product decreased significantly. The SEC trace of the reaction products formed after 3 days at −40 °C (Figure 3c) showed that virtually no three-armed star was formed. However, the size of the one-armed signal indicated some PILi remained unreacted. Accordingly, the tem-

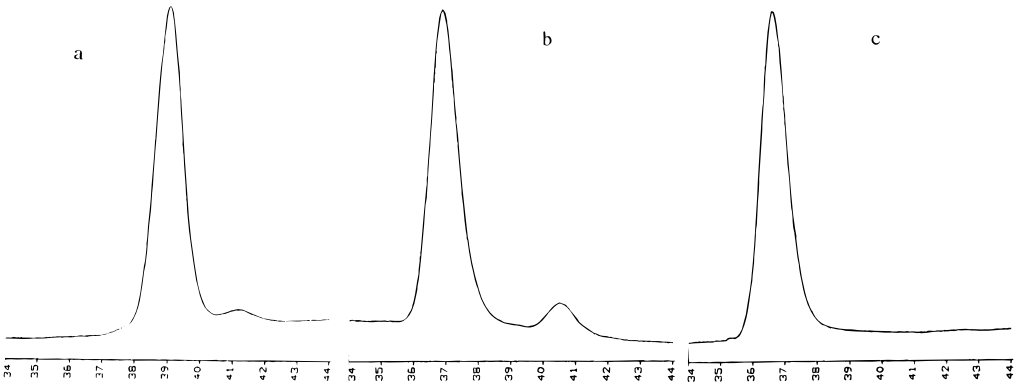

Figure 4. SEC traces taken at different stages during the synthesis of polyisoprene/polybutadiene A_2B_2 star: (a) $(PI)_2Si(PB)_2$; (b) $(PI)_2Si(PB)_2$ after fractionation.

perature was allowed to rise to −30 °C over 6 h and held there for a further day. The SEC trace taken at that point showed a reduction of the size of the one-armed product signal (Figure 3d) but no change in the region where the three-armed star should elute. A sample, taken 2 days after the increase of the temperature showed that no further change had occurred. These results prove clearly that, under these conditions, the reaction stops effectively completely after the addition of the second PI arm. This low-temperature route was employed to synthesize A_2B_2 stars, containing two polyisoprene arms and two polybutadiene arms. After the linkage of two PI arms (Figure 4a) to each silicon atom at −40 °C as described above, a sample of the reaction mixture was taken and analyzed by SEC. An excess of PBLi in cyclohexane was added to the reactor and the temperature was allowed to rise to +20 °C and held there. After 3 days a little triethylamine was added and the reaction was allowed to continue for a further 3 days. Figure 4b shows the SEC trace at that time. The absence of any $(PI)_2SiCl_2$ peak shows that the linking of the PBLi to the silicon center was complete. The remaining excess PB in the crude material was removed by fractionation, leading to the pure A_2B_2 star (Figure 4c). The data for the characterization of the star polymers and their precursors are listed in Table 2.

The molecular weight data for the stars obtained by both routes are in excellent agreement with expectation based on the molecular weights of the parent arms (and in the controlled temperature procedure also with those of the two-armed intermediate). In addition, the composition calculated from the M_n of the arms was found to be in complete agreement with that obtained by ^1H NMR spectroscopy.

Conclusion

In conclusion, the results clearly prove that end-capping PI with styrene to create steric hindrance to multiple substitution of $SiCl_4$ provides a successful approach to the synthesis of A_2B_2 star polymers having uniquely two PI and two PB arms. The same goal can be achieved rather more simply (avoiding the necessity for end-capping) by linking the first two arms at a temperature low enough to create selectivity between the successive steps of replacement of chlorine in $SiCl_4$.

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