CHAPTER VI

Synthesis and Characterization of Linear and Radial Block Copolymers of Styrene and Isoprene through a Novel Coupling Agent by Living Anionic Polymerization

6.1. Introduction

Szwarc and coworkers were first to observed the active anionic nature of growing polymer chains, which they termed as "living" polymers, while studying the polymerization of styrene in tetrahydrofuran using sodium naphthalene as an initiator.[1,2] Living anionic polymerization offered a new tool and the ability to control the course of polymerization, and its discovery and development in the 1950s transformed the synthetic rubber industry. Subsequently, living anionic polymerization has proved itself to be one of the most efficient and widely used systems for the synthesis of homo and block copolymers. This technique has several advantages and is widely used for the preparation of various copolymers with precisely controlled block compositions as well as molecular weights with a narrow molecular weight distribution.[3-11]

Styrenic block copolymers are the most widely used thermoplastic elastomers (TPEs), accounting for nearly 45% of the total TPE consumption worldwide at the end of the twentieth century.[12,13] The polymers possess a distinct molecular architecture with a "hard" thermoplastic segment and a "soft" elastomeric segment. Styrenic TPEs are usually polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS), polystyrene-*b*-poly (ethylene/butylenes)-*b*-polystyrene (SE/BS), and polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS) block copolymers. Living anionic polymerization can be employed in the preparation of these highly useful styrenic TPEs using several different processes that may be classified as either sequential or coupling processes.[14]

Coupling process has a number of advantages over sequential process,[15,16] such as i) symmetrical final product, ii) less interference of impurities with coupling process, and iii) flexibility in the coupling reagents used to prepare radial polymers. Moreover, coupling processes are of great importance in industrial preparations of polymers. Many di- and poly-functional coupling agents[17] (e.g., dihalo compounds, polyepoxides, dianhydrides, chlorosilanes, carbon dioxide/disulfide, halides and mixed halides, monoesters such as benzoates or acetates, divinylbenzene, adipates/terephthalates, and vinylhalomethylarenes) have been employed for the synthesis of linear and radial block copolymers. Recently, a unique coupling agent, malonyl chloride (MC), was used by our group for synthesizing miktoarm star copolymers[18] and amphiphilic coil-rod-coil triblock copolymers[19] with controlled molecular weights and narrow polydispersity indices (PDI) due to the low reactivity of the amidate anion.

The polystyrene-*b*-polyisoprene (SI) block copolymers have been found to be valuable in diverse applications, and various physical properties of these polymers have been studied.[20,21,22] In this communication, we report the first one-pot synthesis of the three kinds of SI; di-, tri-, and star- (or radial) block copolymers using the living anionic polymerization technique at room temperature with quantitative yields. We have used MC, a bifunctional coupling agent, and a novel *in situ* generated tri-functional coupling agent (MC-1, Scheme 6.1). In spite of using bi-functional coupling agent we obtained star-block copolymer along with the di- and tri- block copolymers at the same time. We have also proposed the most probable mechanism which explains the results and is most logical based on the scientific facts already known. To the best of our knowledge so far there is no report of the formation of a star-block copolymer with the help of a bi-functional coupling agent employing anionic polymerization at room temperature.

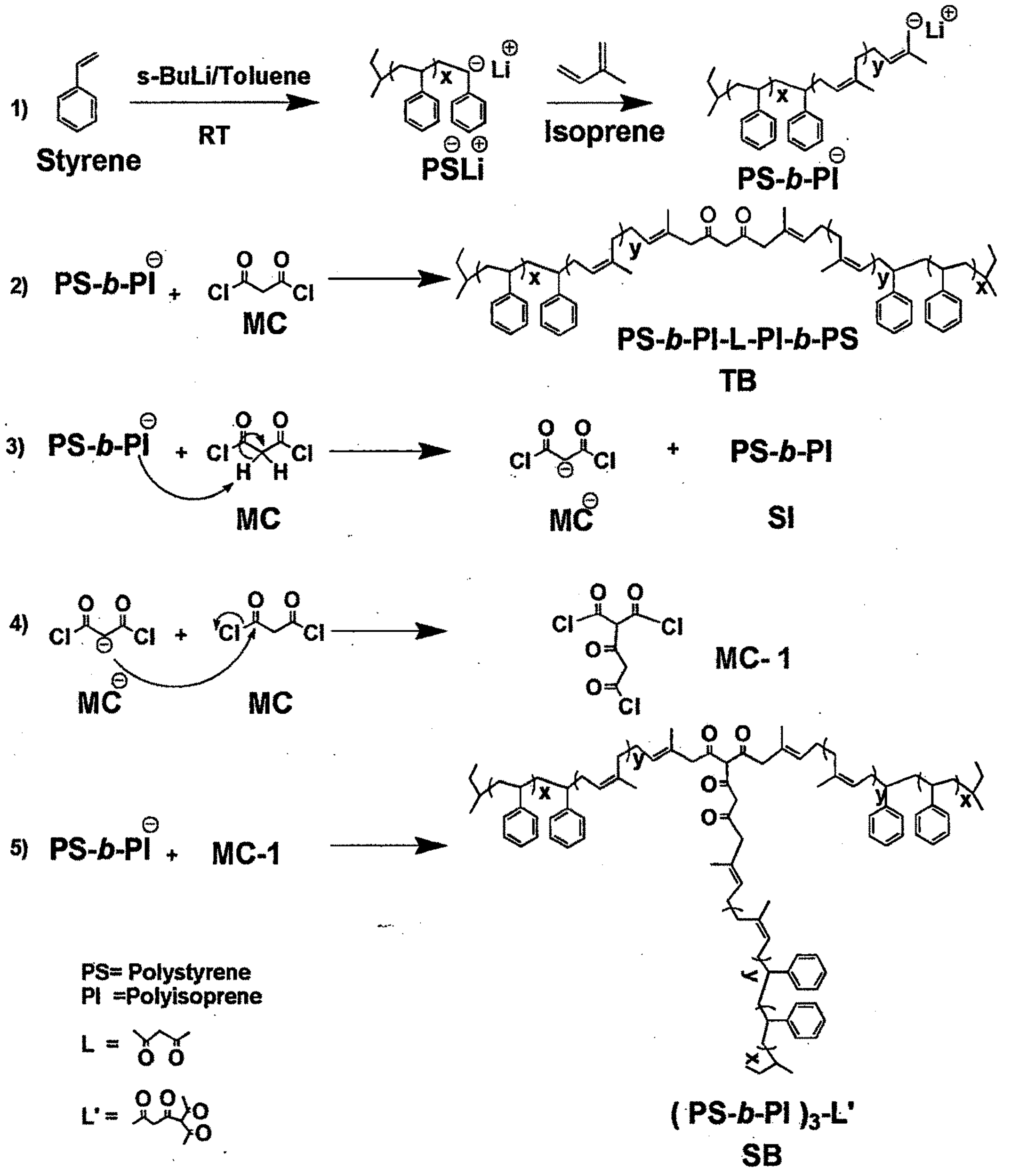
6.2. Experimental

The monomers Styrene (Aldrich, 99%) and Isoprene (Aldrich, 99%) were passed through activated alumina, washed with aqueous solution of sodium hydroxide followed by distilled water to remove inhibitors, dried over calcium hydride and finally distilled under reduced pressure. Malonyl chloride (Aldrich, 97%) was dried over calcium hydride, vacuum distilled, diluted with toluene, and sealed in glass ampoules equipped with break seals. Toluene (Aldrich, 99%) was purified using standard high vacuum-technique described elsewhere.[23,24] The initiator *sec*-butyllithium (*s*-BuLi) (Aldrich, 1.6 M in hexane), calcium hydride (Junsei, 95%), *n*-butyllithium (Aldrich 1.6 M in hexane), and 1,1-diphenylethylene (Aldrich, 97%) were used as received without further purification. .

Elastomeric block copolymers of SI were synthesized in a specially-fabricated glass apparatus using break seals under high-vacuum conditions (10^{-6} Torr) and in an inert atmosphere. The synthesis of sample C3 (1:1, initiator to coupling agent molar ratio) has been described as an example of a typical anionic polymerization. The homopolymerization of styrene (0.84 g, 8.06 mmol) was initiated with the addition of *sec*-butyllithium (*s*-BuLi, 0.011 g, 0.18 mmol) using the break seal technique at room temperature. The color of the reaction mixture turned to deep red-orange[25] indicating the formation of the living polystyryl anion. After allowing this reaction to proceed for 2 h, the second monomer isoprene (0.60 g, 8.84 mmol) was introduced. The color of the reaction mixture changed to light yellow, and copolymerization was allowed to take place for 6 h. After complete consumption of the second monomer, malonyl chloride (0.025 g, 0.182 mmol) was introduced to the living diblock copolymer and it was allowed to react for 1 h. The reaction was terminated by adding argon-purged methanol, and the resulting mixture was poured into a large amount of methanol for complete precipitation. The precipitated polymer was filtered and dried. It was then dissolved in benzene and freeze-dried. Similar procedures were followed for the experiments C1 and C2.

6.3. Methods

For RP-TGIC experiments, C18 bonded silica column (Nucleosil, 500 Å pore, 250 mm × 2.1 mm i.d., 7-μm particle size) was used. The mobile phase was a mixture of CH_2Cl_2 and CH_3CN (58/42, v/v, Samchun, HPLC grade) and the flow rate was 0.25 mL/min. The column temperature was controlled by circulating water from a bath/circulator (Haake, C25P) through a homemade column jacket. The polymer sample was dissolved in the elution solvent (2 mg/mL), and the injection volume was 100 μL. TGIC chromatograms were recorded with a UV absorption detector (Younglin, UV 730D) at a wavelength of 260 nm. For the SEC analysis of the fractionated samples, two mixed bed columns (Polymer Lab. Mixed C, 300 × 8.0 mm i.d.) were used. SEC chromatograms were recorded with a multiangle laser light scattering (Wyatt, mini-DAWN TREOS) and a refractive index detector (Shodex, RI-101) using THF (Samchun, HPLC grade) as a mobile phase. The polymer samples were dissolved in THF, the injection volume was 100 μL, and the flow rate of the mobile phase was 0.8 mL/min. The column temperature was maintained at 40 °C using a column oven (Eppendorf, TC-50).



Scheme 6.1. Synthesis and Mechanism Leading to the Diblock Copolymer (SI), Triblock copolymer (TB), and Star-block Copolymer (SB).

6.4. Results and Discussion

The synthesis of linear di-, tri-, and star-block copolymers (polystyrene-*b*-polyisoprene (SI), polystyrene-*b*-polyisoprene-L-polyisoprene-*b*-polystyrene (TB), and (polystyrene-*b*-polyisoprene)$_3$-L' (SB), respectively) was achieved by anion-initiated polymerization of styrene, subsequent addition of isoprene to the living polystyryl anion, followed by the addition of MC. This sequence resulted in a mixture of all three block copolymers. The living anionic polymerization was carried out with three different molar ratios of initiator to monomer, and led to mixtures of SI, TB, and SB with nearly 100% yield in each case (C1–C3), with controlled molecular weights and narrow PDIs (1.01–1.09) (Table 6.1). The molecular weights of the polymers were determined by size-exclusion chromatography multiangle laser light scattering (SEC-MALLS) after separating them by Reversed Phase Temperature Gradient Interaction Chromatography (RP-TGIC)[26-28] (Table 6.1) technique. The molecular weights determined by this technique are in good agreement with the calculated molecular weights. This technique exhibits much higher resolution than SEC and has been successfully employed for separating polymers of different molecular weights.[29-31] Table 6.1 shows that by changing the molar ratios of the initiator to coupling agent, the weight fractions of various SI block copolymers can be controlled.

Table 6.1. Selected Data for the Synthesis of Diblock Copolymer (DB), Triblock Copolymer (TB), Star-block Copolymer (SB) of Styrene (ST) and Isoprene (IP) Using *sec*-Butyllithium (*s*-BuLi) as an Initiator and Malonyl Chloride (MC) as a Coupling Agent.

Sample	Amount of reagents (mmol)				M_nx10^{-3}		Weight fraction (%)[c]	Yield (%)[d]
	s-BuLi	ST	IP	MC	Calcd[a]	Obsd[b]/PDI[b]		
C1	0.258	8.84	8.93	0.025	DB-5.9	6.00/1.03	80.12	100
					TB-12.0	12.0/1.03	5.34	
					SB-17.9	19.1/1.05	13.88	
C2	0.234	9.42	9.29	0.116	DB-6.9	7.20/1.09	42.25	99
					TB-13.8	14.7/1.02	11.03	
					SB-20.7	21.6/1.01	45.82	
C3	0.180	8.06	8.84	0.182	DB-8.0	8.00/1.02	35.70	100
					TB-16.1	16.4/1.04	20.20	
					SB-24.3	24.0/1.04	40.10	

[a] Number average molecular weight (M_n) was calculated using the relation M_n =Molecular weight of *s*-BuLi + {[styrene]/[*s*-BuLi] × molecular weight of styrene} + {[isoprene]/[*s*-BuLi] × molecular weight of isoprene}. [b] M_n and polydispersity index (PDI) were measured by size-exclusion chromatography multiangle laser light scattering (SEC-MALLS) after fractionation of mixed samples. [c] Weight fractions were calculated using Reversed Phase Temperature Gradient Interaction Chromatography (RP-TGIC), dead polystyrene was not above 4 % (C1-C3). [d] The yield was calculated gravimetrically.

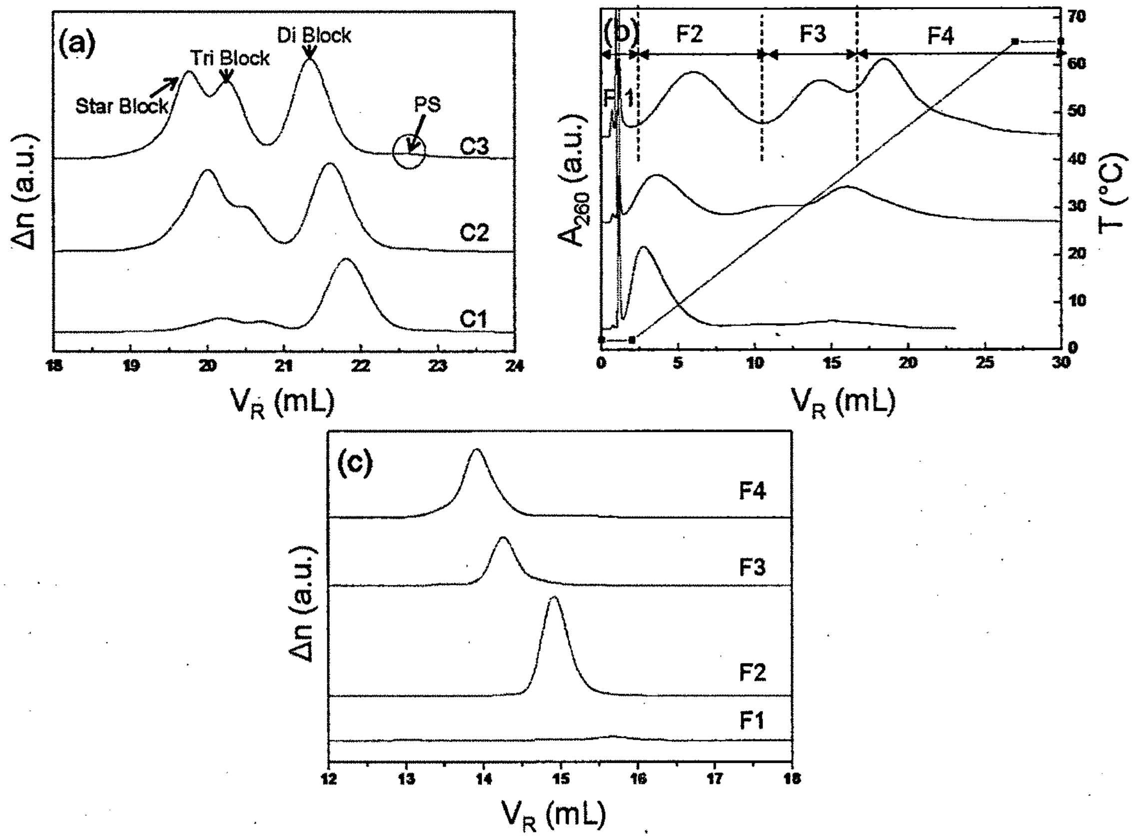


Figure 6.1. (a) Size-exclusion chromatography (SEC) curves of three sets of polymers obtained from C1 to C3. (b) Temperature gradient interaction chromatography (TGIC) curves of the various block copolymers, F1–F4 showing the fractionation (dotted lines) of C3. (c) SEC curves of four TGIC fractions (F1–F4) after fractionation of C3.

Figure 6.1a depicts the SEC chromatograms of the three different kinds of polymers. We can see the existence of the three major products (SI, TB, and SB) in all three sets of polymerization (C1–C3), as well as a minor product (up to 4%) of dead polystyrene (marked with a circle in Figure 6.1a as PS). The latter is formed due to the chain-transfer reactions as reported earlier^{28,29} and its presence was confirmed after fractionation using IC, as shown in Figure 6.1c (F1). In experiment C1, a small amount of the coupling agent MC was introduced in the living diblock anion (1: 0.0969; *sec*-BuLi: MC). The ratio of TB and SB polymers is indicative of the fact that the formation of the anion (MC$^{\ominus}$) is dominating over the coupling, leading to the SB polymer via the *in situ* generated tri-functional coupling agent MC-1 because of the greater reactivity of the methylene group in MC. A large quantity of the living diblock anions remains unreacted leading to the diblock copolymer as the major component in the polymeric mixture. In the experiment C2, when an ideal concentration of the coupling reagent was employed with respect to the living anions (1: 0.495; *sec*-BuLi: MC), the maximum yield of the SB polymer was obtained. The tendency of the anions to react with methylene group *vs.* the acyl chloride remains unchanged. Introduction of an excess of the coupling agent (1: 1.011; *sec*-BuLi: MC) in experiment C3 made MC readily available for the coupling with the anions and the formation of the TB copolymer is increased due to the increased MC: MC-1 ratio. The comparative evaluation of the experiments C1-C3 indicates that the maximum yield of SB is obtained in case of C2 as explained; and TB is formed in a greater amount in the presence of an excess of the coupling agent while a low proportion of the coupling agent leads the polymer composition having higher content of SI block polymer.

Figure 6.1b displays RP-TGIC chromatograms of all the three samples and fractionation of C3. These chromatograms show three to four distinct peaks for the polymers. Under the RP-TGIC conditions, polyisoprene (PI) interacts with the stationary phase more strongly than PS. The retention of the SI block copolymer species increases as the absolute molecular weight of PI block component increases. Therefore, the elution sequence under these conditions is: di-, tri-, and star-block copolymer.

To identify the species corresponding to each elution peak, RP-TGIC elution peaks of sample C3 were fractionated as marked with dotted vertical lines (Figure 6.1b), and these fractions were characterized by SEC for the determination of absolute molecular weight. SEC chromatograms of the TGIC fractions (F1-F4) are depicted in Figure 6.1c, and their individual SEC values (Table 6.1) indicate that the molecular weights of tri- and star-block copolymers are increasing to two- and three-fold, respectively, compared to that of the diblock copolymer. The chromatograms illustrate a shift to the higher molecular weights from F1–F4, and this data confirms the formation of the block copolymers.

Scheme 6.1 illustrates the route leading to the concurrent synthesis of various block copolymers. It also depicts the proposed mechanism for the formation of the new coupling agent (MC-1), leading to the novel synthesis of the star-block copolymer. With the introduction of the MC into the living diblock anion, the coupling agent (MC) undergoes substitution reaction at both ends to form the linear triblock copolymer, TB (Step 2). At the same time, the living anion may abstract a proton from the active methylene group of MC, giving a new resonance stabilized anion ($MC^{\ominus}$) and terminating the living polymer to give the diblock copolymer SI (Step 3). The anion $MC^{\ominus}$ then reacts with another molecule of the coupling agent MC in a nucleophilic substitution reaction leading to the coupled malonyl chloride (MC-1, Step 4). The reaction of the living diblock anion with this *in situ* generated tri-functional coupling agent MC-1 is leading to the synthesis of the star-block copolymer having three arms (Step 5). This mechanism satisfactorily explains the simultaneous formation of SI, TB, and SB. Furthermore, after RP-TGIC a very small hump is observed indicating the presence of a minute quantity of a higher molecular weight polymer (Figure 6.1b, $V_R \sim 24$ mL). This suggests that the mechanism proposed can be extended leading to *in-situ* formation of minute amounts of the four armed, tetra-functional coupling agent.

6.5. Conclusions

A novel, cheap and readily available coupling agent has been successfully employed in the anionic polymerization at room temperature leading to the concurrent synthesis of the three different block copolymers; di-, tri-, and star-block polymers of polystyrene-*b*-polyisoprene. High degree of control over the molecular weight and weight fractions of various SI block copolymers has been demonstrated by changing the molar ratios of initiator to the coupling agent. A new tri-functional coupling agent (MC-1) is generated *in situ* leading to the star-block copolymer. The present results have encouraged us to continue to investigate the mechanical and thermal properties of these polymers having different compositions and to further study the application of the coupling agent in controlling the weight fractions of each block copolymer.

6.6. References

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