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ORIGINAL PAPER

Synthesis of novel styrene-olefin triblock copolymer via living anionic polymerization

Mohammadreza Jozaghkar and Farshid Ziaee*

Department of Polymer Science, Iran Polymer and Petrochemical Institute, Tehran, Iran

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ABSTRACT

Innovative strides in polymer synthesis have led to the successful living anionic polymerization of styrene-olefin triblock copolymers, yielding varying molecular weights and a remarkably narrow dispersity (Đ) in cyclohexane solvent at 45°C, initiated by n-butyllithium. The novel approach employs anionic polymerization, augmented by the aid of a coupling agent known as 1,12-dibromododecane. Unlike traditional alcohol-based methods employed in polystyrene synthesis, this coupling agent, introduced at the end of the reaction, grafts two living macro-styrene chains with the dodecane chain, effectively acting as the pivotal second component in the formation of the triblock copolymer. Extensive experimentation pinpointed 45°C as the optimal temperature for anionic copolymerization in cyclohexane solvent. The comprehensive analysis, encompassing ^{13}C NMR, ^{1}H NMR, FTIR spectroscopy, and GPC, confirms the successful synthesis of styrene-dodecane-styrene triblock copolymer. The NMR results illustrate successful molecular structures, while GPC attests to the precision, showing a narrow Đ of below 1.2. This pioneering approach not only underscores the efficiency of anionic polymerization in the synthesis of styrene-olefin-styrene triblock copolymer using termination strategy but also promises extensive implications in material science and industrial applications. **Polyolefins J (2024) 11: 95-101**

Keywords: Living anionic polymerization; polystyrene; styrene-olefin-styrene triblock copolymer; 1,12-dibromododecane.

FINTRODUCTION

The technique of living anionic polymerization is regarded as an unparalleled technique in the realm of polymer synthesis, providing an unparalleled level of control over polymer architecture, molecular weight, and Đ. This method has emerged as a pivotal way, enabling the creation of polymers with remarkable precision and narrow Đ, all achievable under moderate reaction temperatures [1-3]. Its applicability spans various monomers, demonstrating remarkable efficiency, especially in nonpolar compounds such as styrene and dienes. It is adept at accommodating and stabilizing negative charges within active centers [4,5]. The advent of living anionic polymerization in the realm of styrene-based polymers heralds a transformative era characterized by supreme precision and structural control. Unlike conventional methods, this technique offers an unprecedented level of mastery over the polymerization process. It enables scholars to dictate the growth, composition, and architecture of the polymer with exceptional accuracy, leading to materials with

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*Corresponding Author - E-mail: f.ziaee@ippi.ac.ir tailored properties and functionalities [6-8]. Styrene, a fundamental component of polymer chemistry due to its versatility and advantageous properties, undergoes a transformation in its potential when subjected to living anionic polymerization. This method ensures a controlled, uninterrupted chain growth, allowing for the creation of intricate and specialized structures [9,10]. By precisely regulating the addition of monomers and controlling reaction conditions, the resulting polymers exhibit enhanced uniformity and predictability, setting them apart from their conventionally synthesized counterparts [11,12]. Central to this pioneering method is the ingenious use of 1,12-dibromododecane coupling agents to introduce linear, soft olefin unit into rigid styrene block. This agent can be introduced at the end of the reaction and plays a crucial role in the formation of styrene-based copolymers. Its role in linking macrostyrene chains leads to the creation of unique co- and ter-polymers, thereby expanding the spectrum of available materials with tailored properties. Crucially, the adding of 1,12-dibromododecane coupling agent at the end of reaction provides a golden opportunity to tailor-made the molecular weight of polystyrene blocks. It not only diversifies the molecular architecture of the synthesized polymers but also contributes significantly to achieving a remarkably narrow molecular weight distribution.

This investigation endeavors to synthesize styrene-dodecane-styrene (SDS) triblock copolymers utilizing a tailored process in cyclohexane solvent maintained at 45°C, employing n-butyllithium as an initiator and 1,12-dibromododecane as a coupling agent. Comprehensive characterization of the synthesized polymers delves into elucidating not only their molecular weight but also their microstructure. This characterization is executed through meticulous analysis employing advanced spectroscopic techniques including ^{13}C NMR, ^{1}H NMR and FTIR. These techniques afford invaluable insights into the molecular intricacies, offering a profound understanding of the synthesized block copolymer structural composition and configuration.

EXPERIMENTAL

Materials

Essential chemicals and reagents, comprising the high-quality styrene monomer (purity: 99%), n-butyllithium initiator (2.0 M in cyclohexane), sec-butyllithium initiator (1.4 M in cyclohexane), 1,12-dibromododecane terminating agent (purity: 99.5%), cyclohexane solvent (purity: 99%), concentrated sulfuric acid (purity: 98%), and calcium hydride powder (purity: 95%), were procured from Merck, Germany.

Living anionic polymerization

In the process of conducting living anionic polymerization, meticulous steps were followed under an inert Ar atmosphere. To ensure the purity of styrene, it underwent thorough purification using calcium hydride powder over several days to eliminate any dissolved water. The purified styrene was then meticulously vacuum-distilled at 50 mmHg and 60°C, carefully collecting it into a specialized monomer buret. Meanwhile, cyclohexane underwent a rigorous purification process, being stirred over concentrated sulfuric acid for an extended period, followed by a meticulous reflux under an inert atmosphere for several hours. Subsequently, the purified cyclohexane was injected into a specially prepared glass container within a vacuum glove box. Precise amount of n-butyllithium and monomer were then introduced into the controlled medium, confirmed by the presence of a distinct colored solution, validating complete purification of the system. Once confirmed, the solution within the glass container was seamlessly transferred to the polymerization reactor, carefully maintained within a thermostatic water bath set at a precise temperature of 45°C ± 0.1°C under the protective shield of an Ar atmosphere. The entire polymerization setup is based on our previous work [13]. Initiation of the polymerization process commenced with the addition of purified monomer, while termination occurred precisely after 4.5 hours, employing degassed 1,12-dibromododecane. Various triblock copolymers with different molecular weights were synthesized, and their successful synthesis was compared with the synthesized polystyrene (refer to Table 1). Figure 1 illustrates chemical structure of the synthesized triblock copolymer.

Table 1. The molecular weight and Đ of the synthesized samples.

Sample code	Type	M_n×10$^{3(a)}$	M_n×10$^{3(b)}$	Đ
PS	Homo-polystyrene	1.43	1.61	1.11
SDS3	styrene-dodecane-styrene	0.79	0.83	1.09
SDS5	styrene-dodecane-styrene	1.21	1.32	1.07
SDS7	styrene-dodecane-styrene	1.70	1.81	1.15

(a) Measured by GPC
(b) Measured by ^{1}H NMR

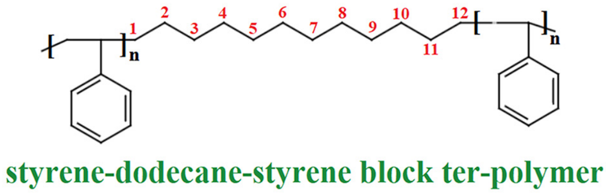


Figure 1. Chemical structure of styrene-dodecane-styrene triblock copolymer synthesized via living anionic polymerization.

Characterization

GPC

For Gel Permeation Chromatography (GPC) analysis, the examination was conducted in tetrahydrofuran (THF) at a flow rate of 1 mL/min, utilizing an Agilent 1100 system (USA). This system was fitted with a differential refractometer detector and a PLgel 5 µm OH-MIXED C 300 × 7.5 mm column containing Agilent PS standard, maintained at a constant temperature of 30°C. The solution's concentration employed for this analysis was set at 1 g/L.

NMR

In order to Nuclear Magnetic Resonance (NMR) analyzing, sample solutions underwent analysis using a Bruker Avance 400 MHz spectrometer from Germany. For ^{13}C NMR, the samples were at approximately 20% (w/v) concentration, while ^{1}H NMR used a 5% (w/v) concentration. Both solutions were contained within a 5 mm NMR tube, maintained at 20°C. The ^{1}H NMR analysis encompassed a scan over 32 K data points, covering a spectral width of 16 ppm. Parameters included an acquisition time of 1.59 s, a relaxation delay of 10 s, a pulse width of 30°, and a total of 4 scans. Meanwhile, the ^{13}C NMR spectra comprised 64 K data points, with a spectral width of 220 ppm, an acquisition time of 1.59 s, a relaxation delay of 2 s, a pulse width of 90°, and an extensive scan involving 20,000 repetitions.

FTIR

Characterization of the synthesized samples was also carried out by a FTIR Bruker-IFS48 (Germany) spectrometer in the wavenumber range of 4000-400 cm^{-1}.

RESULTS AND DISCUSSION

Presence of flexible olefin units in styrene co- and ter-polymers significantly affects the physical properties of final products [14-16]. It has been shown that the presence of flexible units such as butadiene play pivotal role on the attributes and application of styrene-based co- and ter-polymers [17-19]. Various methods have been investigated to produce these kinds of incredible copolymers. Most of them are based on sequential addition of comonomers. For instance, Wei and coworkers [20] synthesized styrene-butadiene-styrene triblock copolymer latex using RAFT miniemulsion polymerization. It should be pointed out that the styrene conversion in this method was about 80%, resulting in small transition copolymer segment with gradient composition formed between the first block and the second block. Wu *et al.,* [21] reported the synthesis of in-chain multi-functionalized random butadiene-styrene copolymer via anionic copolymerization. In their attempts, they used 1,1-bis(4-dimethylaminophenyl)ethylene and the product for carbon black-based composite. In their study, they synthesized the aforementioned copolymers through the addition of comonomers, which led to the difficulty in controlling the styrene units in the copolymers. However, in this particular study, our group has attempted to introduce a much more straightforward strategy for the synthesis of styrene-olefin-styrene triblock copolymers containing controlled styrene units. This cutting-edge strategy helps us to introduce terminating agent into the polystyrene chain and graft two living polystyrene chains, resulting in increasing flexibility of polystyrene, and might consider it as an alternative of TPE product [22,23]. Considering stoichiometry ratio of coupling agent plays major role in successful synthesis of the triblock copolymer without any side reaction [24]. This novel strategy also provides a golden opportunity to synthesize the triblock copolymer at reasonable temperature, alleviating the difficulty of working at negative media temperature.

FTIR

It is well-known that FTIR spectroscopy is one of the simplest, robust and powerful characterization techniques to elucidate the structure and composition of the polymers. Figure 2 demonstrates FTIR spectra of PS and SDS7 samples. The peaks appeared in the region 3150-3050 cm^{-1} are related to the aromatic C-H stretching vibration absorptions. While peaks in the region 3000-2850 cm^{-1} are corresponded to asymmetric and symmetric stretching vibrations of methylene group -CH$_2$, respectively. The weak combination and overtone absorptions are appeared in 2000-1665 cm^{-1}

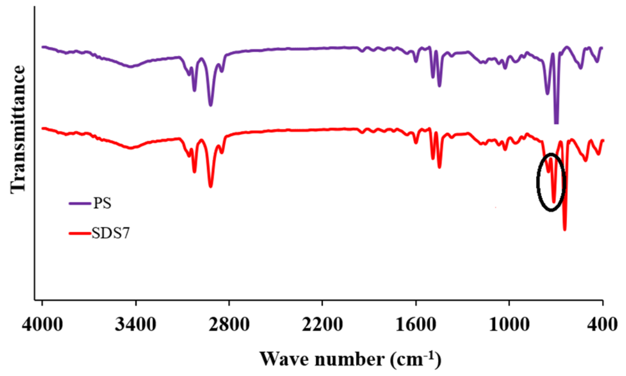


Figure 2. FTIR spectra of polystyrene (PS) and styrene-dodecane-styrene triblock copolymer (SDS7).

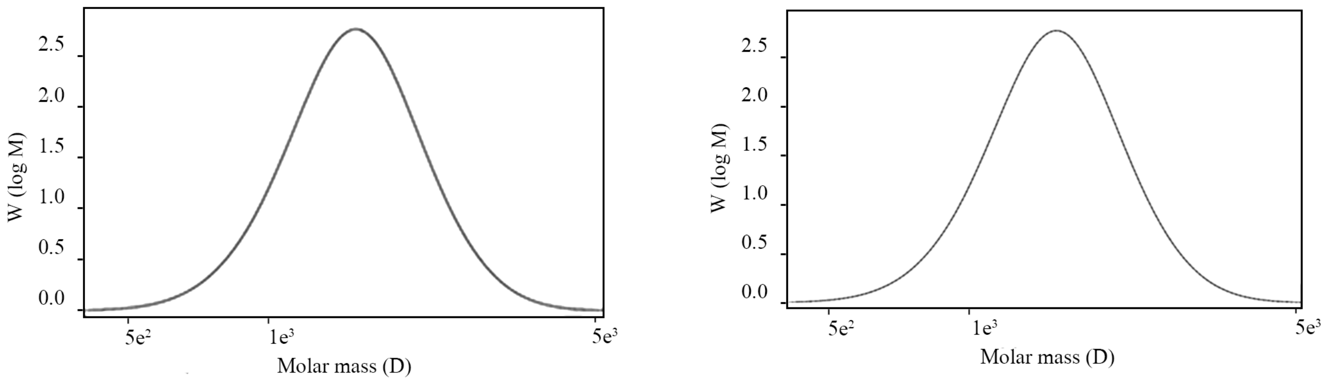
range. The absorption peaks at wavenumbers of about 1630, 990, and 910 cm^{-1} may be corresponded to the same new combination for low molecular weight polystyrene. The absorption peak at the wavenumber of 1370 cm^{-1} is corresponded to methyl C-H of initiator. The characteristic absorption peaks at the wavenumbers of 756 cm^{-1} and 698 cm^{-1} are attributed to C-H out-of-plane bending absorptions. Along with the mentioned peaks, CH_2 rocking peak appeared at 720 cm^{-1}, and absence of alkyl halide C-H sharp peaks at 1291 and 1230 cm^{-1} represents successful synthesis of styrene-dodecane copolymer [13].

GPC

In Figures 3a and 3b, the GPC spectrum unveils critical insights into the synthesized homo- and triblock copolymer. As a general and accepted rule, the symmetrical GPC curve and the low Đ in controlled polymerization represent the great-controlled characteristics of the samples [25, 26]. As it notably can be seen from Figure 3, the results demonstrate a remarkably narrow molecular weight distribution for both polystyrene and styrene-dodecane-styrene triblock copolymer, indicative of a precisely controlled synthesis process. The molecular weight and Đ of polystyrene and the synthesized triblock copolymers are listed in Table 1. The results underscore the homogeneity and consistency of the polymer chains within this system. These findings affirm not only the successful synthesis of the material but also validate the meticulous uniformity achieved in the triblock copolymers structure. All samples show Đ and molecular weights close to the theoretical calculations. The consistency of M_n data obtained from GPC and ^{1}H NMR tests endorsed good reliability of the quantitative NMR analysis. The slight difference in molecular weights between GPC and ^{1}H NMR results is due to overlap of $CDCl_3$ and aromatic proton peaks [13].

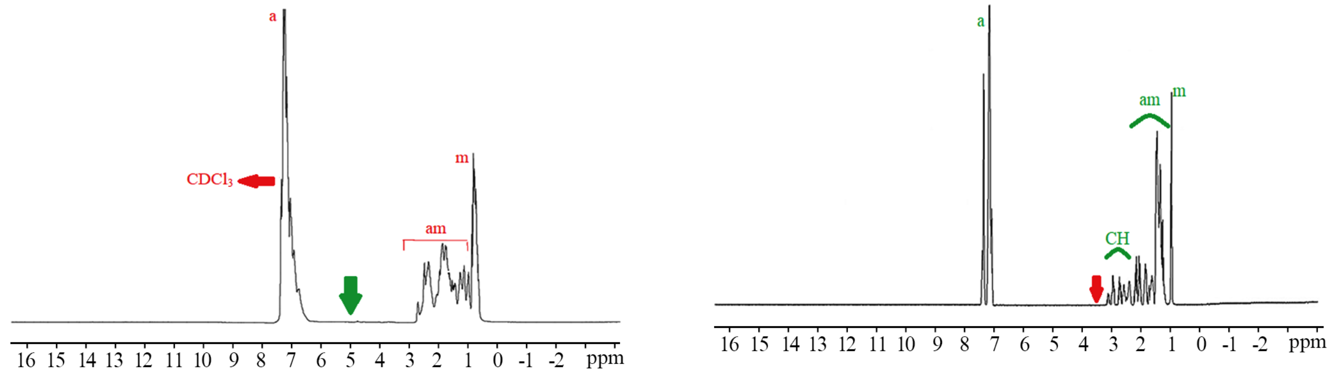
^{1}H NMR

The ^{1}H NMR spectrum of synthesized PS is depicted in Figure 4a. As it can be seen from the Figure 4a, the peak in the range of 0.7-0.9 ppm is corresponded to the protons of methyl groups, assigned with “m”. Moreover, aromatic proton with assignment of “a”, and protons of aliphatic methine and methylene groups “am” have appeared in the range of 6.2-7.3 ppm and 0.8-2.8 ppm, respectively. The successful synthesis of PS without any unreacted monomer is endorsed by absence of three peaks of doublet of doublet in the chemical range of 4-6 ppm. Figure 4b illustrates ^{1}H NMR spectrum of SDS3. As it can be seen, protons of CH_2 groups of the initiator, polystyrene, and dodecane have appeared in the range of 1-2.3 ppm and protons of CH groups of styrene blocks have appeared in the range of 2.3-3.1 ppm. The peaks in the range of 7-7.6 ppm correspond to the



(a) (b)

Figure 3. GPC spectrum of the synthesized sample through living anionic polymerization at 45°C, (a) PS, (b) SDS7.

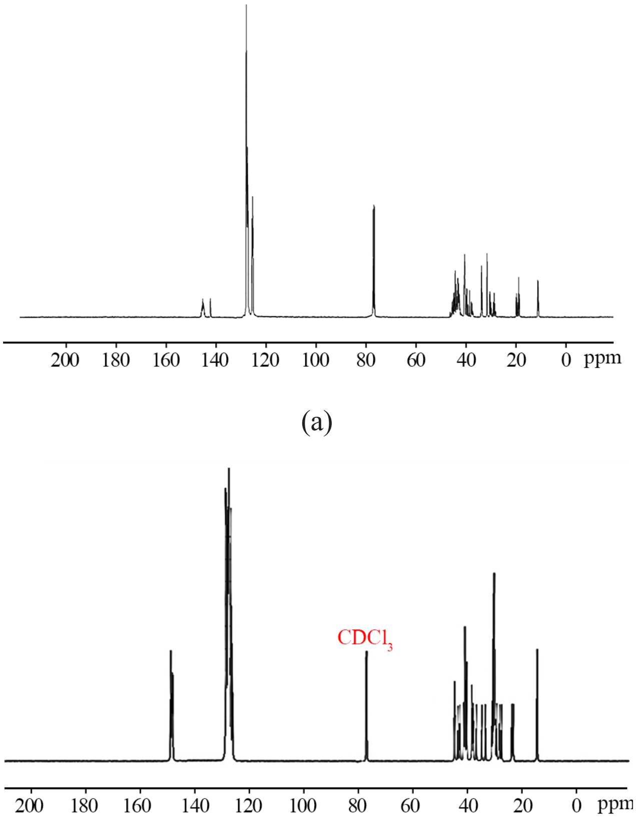


(a)

(b)

Figure 4. ^{1}H NMR spectrum of the synthesized sample through living anionic polymerization at 45°C, (a) PS (b) SDS3.

protons of benzene ring and chloroform. Notably, the absence of a peak at about 3.30-3.50 ppm chemical shift signifies the lack of protons from the CH_2 group bound to bromine, indicating the successful reaction of all binding agents and the absence of unreacted 1,12-dibromododecane as well as reacted one from one side. In this study, quantitative NMR analysis is used to determine M_n of the synthesized homopolymer and triblock copolymers trusting to the fact that this method is reliable for low molecular weight and medium molecular weight samples. As a matter of fact, by increasing molecular weight, the accuracy of integration of molecular weight of polymers alleviates due to inability to detect the end groups [13, 27].



(a)

(b)

Figure 5. ^{13}C NMR spectrum of the synthesized sample through living anionic polymerization at 45°C, (a) polystyrene (b) styrene-dodecane-styrene triblock copolymer.

^{13}C NMR

Figure 5 presents the ^{13}C NMR spectrum of the styrene-dodecane-styrene triblock copolymer, unveiling distinct chemical shifts. The carbons within the benzene ring appear within the chemical shift range of 142-149 ppm. Moreover, the initiator terminal CH_3 group could be identified at a chemical shift of 14 ppm, while the CH groups associated with grafted polystyrene were observed within the range of 41.44-44.57 ppm. Additionally, the spectrum reveals CH_2 signals attributed to styrene units, initiator, and dodecane in the range of 23.00-39.61 ppm. Remarkably, the absence of a peak corresponding to the CH_2 connected to bromine in high fields confirms the prosperous synthesis of styrene-dodecane-styrene triblock copolymers [13].

CONCLUSION

The groundbreaking utilization of living anionic polymerization in the synthesis of styrene-olefin-styrene triblock copolymers has yielded exceptional outcomes. Through meticulous control of reaction parameters, including temperature and coupling agents, this innovative process has demonstrated remarkable control over molecular weight and achieved an impressively narrow Đ of below 1.2. The successful formation of the styrene-dodecane-styrene triblock copolymer, as validated by rigorous spectroscopic and chromatographic analyses, underscores the precision and uniformity achieved in the polymers structure. This pioneering approach not only highlights the effectiveness of living anionic polymerization but also heralds promising implications across diverse realms, ranging from advanced materials science to far-reaching industrial applications, setting a new standard for precision polymer synthesis.

CONFLICTS OF INTEREST

The authors declare that they have no conflicts of interest.

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