ORIGINAL PAPER

Controlled polymerization route to novel α-methyl styrene – olefin triblock copolymers with tailored architecture

Fakhrossadat Mirtaleb[1], Mohammadreza Jozaghkar[2], Farshid Ziaee[2,*]

[1]Department of Biomedical Engineering, Iran polymer and petrochemical institute, Tehran, Iran

[2]Department of Polymer Science, Iran Polymer and Petrochemical Institute, Tehran, Iran

[*]Corresponding author: Email: f.ziaee@ippi.ac.ir

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ABSTRACT

In this study, well-defined α-methyl styrene – olefin triblock copolymers were synthesized via living anionic polymerization using alkyl lithium as an initiator and 1,12-dibromododecane as a coupling agent. The polymerization was conducted in cyclohexane under an inert atmosphere at moderate temperature, allowing for precise control over the molecular architecture and narrow molecular weight distribution. Gel permeation chromatography (GPC) revealed monomodal elution curves with dispersity values close to unity, confirming the living nature of the polymerization process and the high structural homogeneity of the resulting copolymers. Structural characterization was performed using ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy. The ^{1}H NMR spectra confirmed the successful formation of block copolymers through the identification of characteristic chemical shifts corresponding to the initiator, αMS blocks, and central dodecane units. Notably, the absence of brominated end-groups in the spectrum supports complete coupling and high end-group fidelity. Furthermore, ^{13}C NMR analysis revealed well-defined chemical shifts associated with aromatic, methine, and methylene carbons. The disappearance of signals corresponding to bromine-bound methylene carbons confirmed the full consumption of the coupling agent and the effective formation of the triblock structure. These findings validate the successful synthesis of αMS-based triblock copolymers with a high degree of control over molecular parameters, establishing a robust foundation for tailoring thermomechanical and morphological properties for advanced material applications.

Keywords: α-methyl styrene; living anionic polymerization; α-methyl styrene – olefin triblock copolymer; NMR; tailored architecture.

INTRODUCTION

Living anionic polymerization is widely recognized as one of the most powerful techniques in polymer synthesis, offering exceptional control over polymer architecture, molecular weight, and dispersity (Đ). This method has become a cornerstone in precision polymer chemistry, enabling the synthesis of well-defined polymers with narrow molecular weight distributions (MWD) under relatively mild reaction conditions [1–3]. Its effectiveness is particularly notable with nonpolar monomers such as styrene and dienes, where it demonstrates high efficiency and reproducibility. Recently, Dai and coworkers [4] investigated the copolymerization behavior of 1,3-pentadiene and αMS in a living anionic system. Jozaghkar et al. [5] suggested that the stereohinderance of pendant group in αMS results in spatial segregation and formation. They also reported that the poly(α-methyl styrene) synthesized by living anionic polymerization is much closer to the ideal random case than those synthesized via photopolymerization. Hahn and coworkers [6] reported that living anionic copolymerization of styrene and 1-vinylcyclohexene results in a weak gradient structure with monomer reactivity ratios of 2.55 and 0.39 for styrene and 1-vinylcyclohexene, respectively. In a recent attempt, precise styrene-olefin tri-block copolymers with well-defined molecular weight have been reported using living anionic polymerization. In contrast to conventional polymerization methods, this approach allows for meticulous regulation of polymer chain growth, architecture, and composition. As a result, it facilitates the creation of materials with highly tailored properties and functionalities, marking a major breakthrough in precision polymer design [7, 8].

Poly(α-methyl styrene) (PAMS) is a rigid, amorphous thermoplastic that offers several advantageous properties, including high thermal stability and enhanced mechanical strength due to the steric hindrance provided by the α-methyl group. These characteristics make PAMS an attractive candidate for advanced applications such as high-performance coatings, electronic materials, and radiation-resistant components [9-11]. However, its intrinsic rigidity and relatively low impact strength can limit its processability and ductility. To overcome these limitations, the incorporation of flexible linear olefins, such as ethylene or butene, into the polymer backbone is a promising strategy [12, 13]. Copolymerizing PAMS with such olefins introduces chain flexibility and enhances toughness, while retaining the desirable thermal and structural characteristics of the styrenic segments. This approach not only broadens the application potential of PAMS-based materials but also allows for the fine-tuning of physical properties to meet specific performance requirements. At the core of this innovative approach is the strategic use of an olefin-based coupling agent to incorporate flexible, linear segments into otherwise rigid α-methyl styrene blocks. This olefin is introduced at the end of the polymerization process and plays a pivotal role in the synthesis of α-methyl styrene-based co- and terpolymers. By effectively linking macro(α-methyl styrene) chains, it enables the formation of novel polymer structures with tailored mechanical and thermal properties. Importantly, the late-stage addition of the olefin coupling agent offers a valuable means of controlling the molecular weight of the α-methyl styrene segments [7]. This strategy not only broadens the range of achievable polymer architectures but also contributes to a significantly narrow molecular weight distribution, enhancing the uniformity and predictability of the resulting materials.

This study aims to synthesize α-methyl styrene – dodecane triblock copolymers using a controlled polymerization process conducted in cyclohexane at mild reaction condition, with an alkyl lithium initiator and an olefin-based coupling agent serving to link the polymer chains. The synthesized copolymers are thoroughly characterized to determine their molecular weight and assess their microstructural features. Structural analysis is carried out using advanced spectroscopic techniques, including^{1}H NMR and ^{13}C NMR, which provide detailed insights into the molecular architecture and composition of the resulting block copolymers.

EXPERIMENTAL

Materials

High-purity reagents used in this study included α-methyl styrene monomer (purity: 99%), *n*-butyllithium (2.0 M in cyclohexane), *sec*-butyllithium (1.4 M in cyclohexane), olefin-based coupling agent (1,12 debromododecane, purity: 99.5%), cyclohexane solvent (purity: 99%), concentrated sulfuric acid (purity: 98%), and calcium hydride powder (purity: 95%). All chemicals were obtained from Merck, Germany.

Polymerization

The synthesis of α-methyl styrene-based copolymers via living anionic polymerization was conducted under a rigorously controlled inert argon atmosphere as per our previous study [7]. Shortly, the α-methyl styrene monomer was first dried and then distilled at 60 °C under 50 mmHg and collected in a dedicated monomer burette. Cyclohexane was purified by an acid, followed by refluxing under inert conditions. The purified solvent was transferred into a prepared glass container inside a vacuum glove box. Subsequently, precise amounts of initiators and purified monomer were introduced into the system. The appearance of a characteristic color confirmed the successful removal of impurities and system readiness. The reaction mixture was then transferred into a polymerization reactor maintained in a thermostatically controlled water bath at 45 °C ± 0.1 °C under inert atmosphere.

Polymerization was initiated by the addition of the monomer and terminated after the given time using a degassed olefin-based coupling agent. Various α-methyl styrene – dodecane triblock copolymers with different molecular weights were synthesized as shown in Table 1. Figure 1 demonstrates the representation of the copolymerization of α-methyl styrene – block – dodecane by anionic polymerization. After completion of the reaction, the resulting polymer solution was precipitated by slowly adding into an excess of methanol, which served as a nonsolvent for the polymer but was fully miscible with cyclohexane. This nonsolvent-induced precipitation facilitated the separation of the polymer from the reaction medium, enabling efficient removal of residual monomers, unreacted initiator, and other soluble byproducts. The precipitated polymer was collected by filtration and subsequently dried under vacuum prior to further characterization.

Table 1 Summary of the synthesized copolymers and their molecular weight distribution

Sample name	Copolymer type	Reaction Time (min)	$DP_{\alpha MS/arm}$	$M_n \times 10^{3a}$	$M_n \times 10^{3b}$	D
PAMS	Poly(α-methyl styrene)	10.0	13.13	1.61	1.71	1.14
ADA1	α-methyl styrene – dodecane triblock copolymer	1.5	2.27	0.82	0.98	1.19
ADA2	α-methyl styrene – dodecane triblock copolymer	2.5	3.96	1.22	1.32	1.02
ADA3	α-methyl styrene – dodecane triblock copolymer	5.0	6.42	1.80	1.93	1.09
ADA4	α-methyl styrene – dodecane triblock copolymer	7.0	8.49	2.29	2.33	1.11

(a) Measured by GPC

(b) Measured by ^{1}H NMR

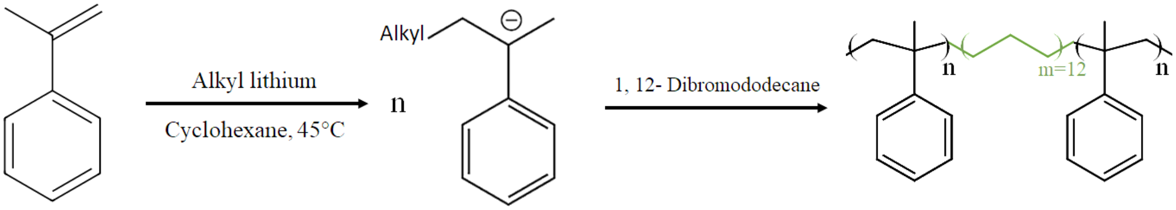

Figure 1. Representation of the copolymerization of α-methyl styrene - dodecane - α-methyl styrene by anionic polymerization.

Characterization

Gel Permeation Chromatography (GPC)

Molecular weight and molecular weight distribution were determined using Gel Permeation Chromatography (GPC) performed on an Agilent 1100 system (USA) equipped with a differential refractive index detector and a PLgel 5 µm OH-MIXED-C column (300 × 7.5 mm). The measurements were conducted at 30 °C using tetrahydrofuran (THF) as the eluent at a flow rate of 1 mL/min. Polystyrene standards were used for calibration, and the sample concentration was 1 g/L.

Nuclear Magnetic Resonance (NMR)

Structural analysis was carried out using a Bruker Avance 400 MHz NMR spectrometer (Germany). For ^{1}H NMR, samples were prepared at a concentration of 5% (w/v) and analyzed in 5 mm NMR tubes at 20 °C. The ^{1}H NMR spectra were recorded with 32 K data points over a spectral width of 16 ppm, using an acquisition time of 1.59 s, a relaxation delay of 10 s, a 30° pulse angle, and 4 scans.

For ^{13}C NMR, the sample concentration was approximately 20% (w/v). Spectra were acquired with 64 K data points over a 220-ppm spectral width, an acquisition time of 1.59 s, a 2 s relaxation delay, a 90° pulse angle, and 20,000 scans.

RESULTS AND DISCUSSION

Controlled polymerization enables precise manipulation of block length and sequence, which is essential for tuning the physical and mechanical characteristics of the resulting copolymers [1]. The introduction of α-methyl styrene as a terminal block offers enhanced thermal stability and rigidity compared to traditional styrenic polymers, expanding the potential application range for these materials [14]. This approach addresses the growing demand for advanced polymers in high-performance applications, where both processability and end-use properties can be tailored at the molecular level. The incorporation of the olefinic segment as the central block in the triblock architecture is a key feature that imparts unique and valuable properties to the copolymer. Olefin blocks, such as those derived from ethylene, butadiene, or isoprene, provide flexibility, elasticity, and impact resistance, effectively acting as a soft phase between the more rigid α-methyl styrene end blocks [11, 15].

The ability to introduce a straightforward approach to synthesize α-methyl styrene – olefin triblock copolymers with tailored architectures opens new avenues for the development of next-generation thermoplastic elastomers and specialty materials. These copolymers can be engineered for a wide array of applications, including automotive parts, adhesives, sealants, and impact-resistant plastics. The combination of controlled polymerization and strategic block selection enables the fine-tuning of properties such as glass transition temperature, modulus, and compatibility with other polymers or additives. As a result, this work not only demonstrates the feasibility of creating novel materials with controlled αMS segment but also establishes an innovative strategy for synthesizing block copolymers using terminating agents. The strategic placement of olefin segments can bridge the gap between conventional plastics and rubbers, offering a unique combination of processability, durability, and performance that is highly sought after in advanced manufacturing sectors [16, 17]. The stoichiometric ratio of the coupling agent is a critical factor in the successful synthesis of triblock copolymers, ensuring minimal side reactions [18]. This innovative approach also offers a significant advantage by enabling the synthesis to proceed at moderate temperatures, thereby eliminating the challenges associated with conducting reactions under sub-zero conditions.

GPC

Figures 2a and b present the GPC chromatograms of the synthesized PAMS and the corresponding α-methyl styrene – dodecane (ADA4) triblock copolymer. These chromatograms provide critical insight into the molecular uniformity and distribution characteristics of the synthesized polymers. For the comparison, the GPC chromatograms of all samples are presented as supplementary materials. In the context of living anionic polymerization, the appearance of a symmetrical and unimodal GPC curve, along with a low dispersity (Đ) value close to unity, is a sign of well-controlled polymer growth [19,20]. Such features confirm the absence of side reactions such as termination or chain transfer during polymerization, thereby affirming the living nature of the process.

From the Figure 2, it can be seen that both homopolymer and block copolymer (sample ADA4) display symmetrical, unimodal peaks, indicating a high degree of uniformity and absence of chain branching or residual precursors. The clear shift to lower retention time for ADA4 compared to PAMS confirms the increase in molecular weight after coupling, supporting successful triblock formation. The M_n determined by GPC, as listed in Table 1, ranges from 0.82 to 2.29×10^3 g/mol across samples. The corresponding Đ ranges from 1.02 to 1.19, which are characteristic of a living anionic polymerization system with minimal termination or transfer reactions [21]. The close agreement between GPC-derived M_n and NMR-derived Mn further validates the consistency of the molecular weight data. The absence of high-molecular-weight shoulders or low-molecular-weight tails in the GPC traces supports the efficient coupling reaction using the 1,12-dibromododecane linker, with minimal formation of side products or uncoupled chains [22].

The consistent and narrow molecular weight distributions of the resulting polymers not only validate the effectiveness of the synthetic strategy but also emphasize the structural uniformity achieved. Such uniformity is particularly critical in applications demanding precise mechanical, thermal, or optical properties [23]. The successful synthesis of well-defined αMS-based triblock copolymers demonstrated here confirms the capability of living anionic polymerization to generate advanced polymeric materials with finely tuned characteristics. Moreover, compared to previously reported triblock copolymers synthesized via living anionic polymerization [7, 8, 21], the M_n values and narrow dispersity (Đ < 1.2) of our triblock samples demonstrate equally high or better control over polymer growth. For example, Dai et al. [4] reported triblock systems with Đ values around 1.25–1.35, while our triblocks maintain Đ values closer to unity, indicating enhanced control possibly due to optimized stoichiometry and the bifunctional nature of the 1,12-dibromododecane linker. Similarly, Zhang et al. [8] achieved styrene-based triblocks with Mn around 1.8×10^3 g/mol, but with slightly broader dispersity (~1.22), attributed to incomplete coupling.

In contrast, the triblocks reported in this study consistently demonstrate Đ values as low as 1.02–1.19, with monomodal GPC traces, highlighting a narrower molecular weight distribution and better-defined architecture.

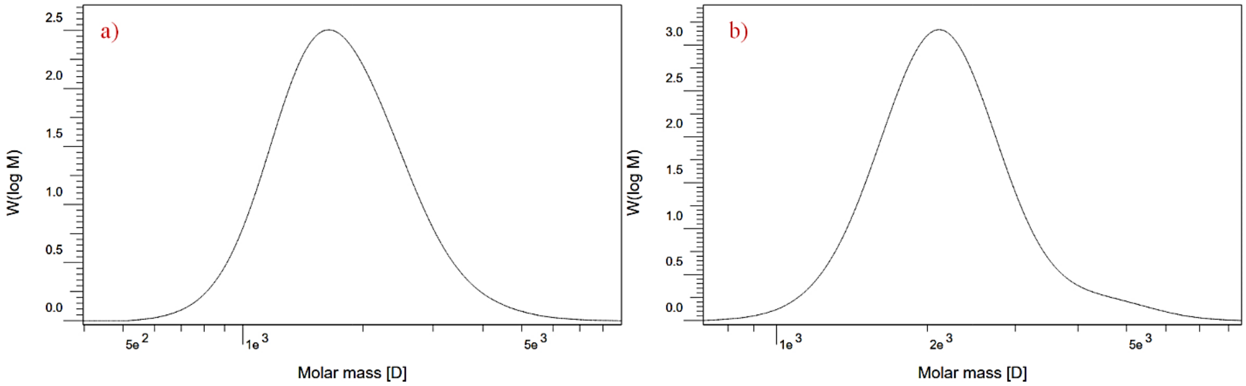

Figure 2. GPC spectrum of the synthesized samples, a) PAMS, b) triblock copolymer ADA4.

^{1}H NMR

Figure 4a presents the ^{1}H NMR spectrum of the synthesized PAMS, revealing distinct signals attributable to its well-defined structure. The resonance appearing in the range of 0.7-0.9 ppm is associated with methyl protons of initiator, while methyl protons of PAMS is appeared in the range of 0.9-1.1 ppm. The aromatic region (6.2-7.3 ppm) displays peaks corresponding to the phenyl protons of the αMS units. Additionally, signals from aliphatic methylene and methine protons are distributed between 0.8 and 2.8 ppm. Notably, the absence of characteristic vinyl proton signals between 4.0-6.0 ppm confirms the complete consumption of the αMS monomer, validating the high conversion and purity of the resulting polymer [25].

The ^{1}H NMR spectrum of the triblock copolymer (ADA4), shown in Figure 4b, further confirms the successful incorporation of both end blocks and the mid-block. Signals in the 1.1-2.3 ppm region correspond to methylene protons along the backbone and those derived from the dodecane coupling unit (long alkyl chains). Protons on the methine groups of the αMS segments resonate from 2.3 to 3.1 ppm, while aromatic protons from the phenyl rings and residual chloroform-d appear between 7.0-7.6 ppm. Unreacted methylene groups adjacent to terminal bromines (-CH_2Br) typically show the resonance in downfield region (3.30-3.50 ppm) with the triplet peaks due to the de-shielding effect of bromine atoms. Absence of these peaks, strongly indicates that the coupling agent 1,12-dibromododecane has fully reacted, with no detectable unreacted or mono-functionalized species [7].

To further evaluate the polymer structure, quantitative ^{1}H NMR analysis was conducted to estimate the M_n of the synthesized polymers. This method provided reliable data, particularly for low and moderate molecular weight samples. The degree of polymerization (n) for the synthesized samples can be quantitatively estimated by analyzing the ^{1}H NMR spectrum, specifically through the integration ratio between the aromatic proton signals and the terminal methyl group resonance (equations 1 and 2). This comparison allows for an accurate assessment of the number of repeating units within the polymer backbone [25].

$n = (a/5) / (d/3)$ (1)

Once the value of n is determined, the number-average molecular weight (M_n) of the polymer can be calculated using the following equation:

$M_n = (n \times M_0 + M_i) \times 2 + M_d$ (2)

where M_0 represents the molecular weight of the α-methyl styrene repeating unit, and M_i corresponds to the combined molecular weight of the chain-end functionalities introduced by the initiator. M_d corresponds to molecular weight of olefin segment. The NMR-derived M_n values showed good agreement with GPC measurements, supporting the reproducibility and precision of the synthesis. The slight discrepancies between the two measurements can be attributed to the partial overlap of aromatic signals with the residual $CDCl_3$ solvent peak in the ^1H NMR spectrum, which can marginally influence the integration accuracy [22].

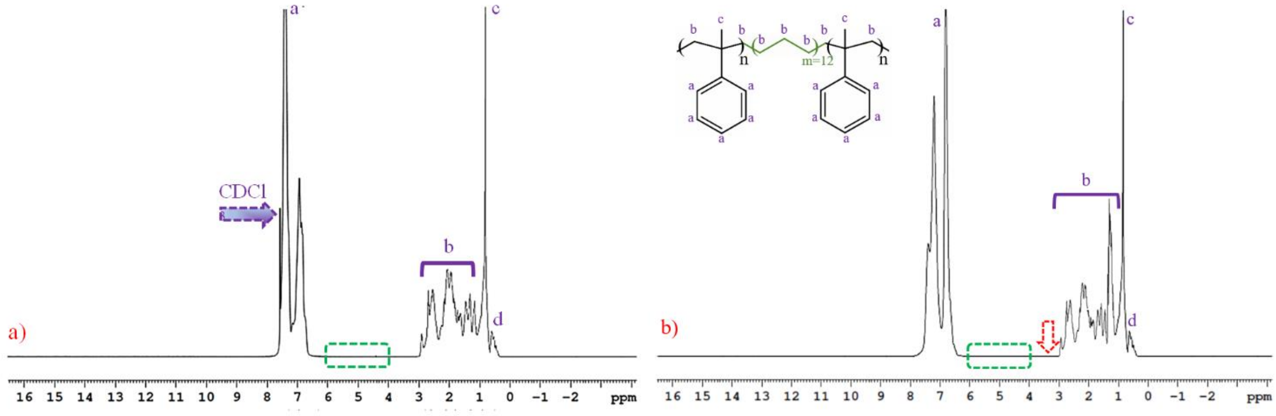

Figure 3. ^1H NMR spectrum of the synthesized samples a) PAMS and b) triblock copolymer ADA4

^{13}C NMR

Figure 4 a and b illustrates the ^{13}C NMR spectrum of the synthesized PAMS and α-methyl styrene – dodecane triblock copolymer (ADA4), providing detailed insight into its molecular structure through distinct carbon resonances. Each segment of the spectrum corresponds to specific components within the polymer chain, confirming successful synthesis and expected block formation [26].

The aromatic carbons associated with the α-methyl styrene units appear in the region of 128-139 ppm, a range typically attributed to the sp^2-hybridized carbons in the benzene ring. The quaternary carbon of benzene ring was appeared in the range of 150-153 ppm. These signals serve as clear evidence for the presence of αMS blocks in the copolymer.

The methyl group at the terminal position of the initiator, likely derived from the initiator, exhibits a distinct resonance around 14 ppm. This signal is particularly important as it provides information about the end-group fidelity, confirming successful initiation of polymerization.

The quaternary aliphatic carbon of the polymerized αMS units is observed between 41.8 and 44.7 ppm. These resonances are characteristic of the tertiary carbon in the α-methyl styrene repeating units, further validating the incorporation of αMS segments into the polymer chain.

In the aliphatic region, signals between 57.2 and 61.8 ppm are attributed to methylene (CH_2) carbons αMS units, the dodecane coupling agent, and the initiator. However, the methylene groups of the coupling agent appeared at a slightly upfield chemical shift compared to those of the αMS units. These overlapping peaks are consistent with the structure of the triblock system and confirm successful incorporation of the flexible dodecane segment between two rigid αMS blocks [24, 5].

Notably, the absence of a distinct resonance peaks near 33-35 ppm, which correspond to $-CH_2Br$, indicates complete reaction and consumption of the 1,12-dibromododecane coupling agent. This observation strongly supports the efficient coupling reaction and formation of the triblock architecture, as no mono-functionalized linker residues are detected [7].

Altogether, the ^{13}C NMR spectrum substantiates the structural integrity of this novel triblock copolymer, reflecting high coupling efficiency, clean chain-end formation, and successful block integration. These findings are in good agreement with the expected chemical structure and support the reliability of the synthetic approach employed.

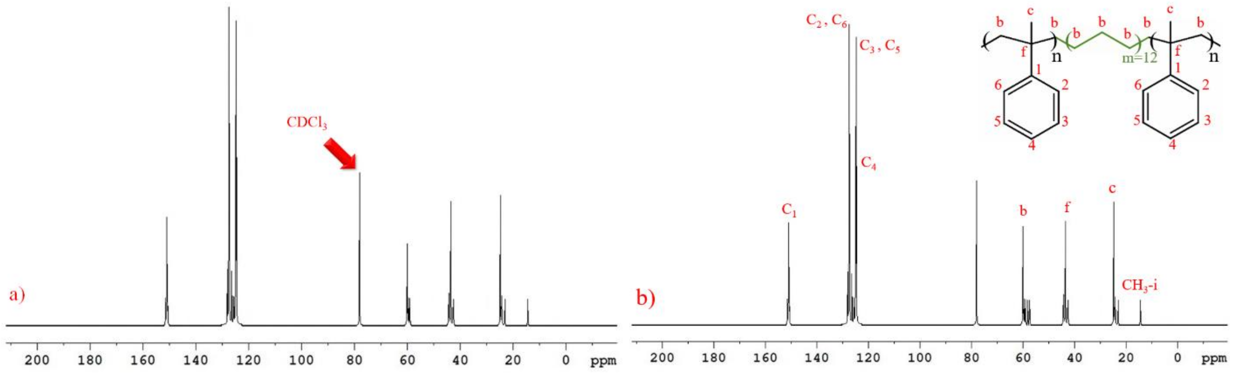

Figure 4. ^{13}C NMR spectrum of the synthesized samples a) PAMS and b) triblock copolymer ADA4.

CONCLUSION

In summary, the successful synthesis of α-methyl styrene – dodecane – α-methyl styrene triblock copolymers were achieved via living anionic polymerization under mild conditions, demonstrating excellent control over molecular weight and architecture. The use of 1,12-dibromododecane as a bifunctional coupling agent effectively linked αMS blocks through a flexible dodecane segment, enabling the formation of symmetric triblock structures with high end-group fidelity. Comprehensive characterization using GPC and NMR spectroscopy confirmed the structural integrity and narrow dispersity of the synthesized copolymers. The absence of signals associated with bromododecane at the chain ends further validated the completeness of the reaction and the living nature of the polymerization process. This synthesis exemplifies the power of this controlled approach in constructing complex macromolecular architectures with predictable and reproducible properties. The strategic placement of olefin segments within the triblock structure provides a model system for studying phase behavior, self-assembly, and structure–property relationships in block copolymers. These materials can bridge the gap between conventional plastics and rubbers, offering a unique combination of processability, durability, and performance that is highly sought after in advanced manufacturing sectors.

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