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Aspects of the Synthesis of Poly(styrene-*block*-isobutylene-*block*-styrene) by TiCl_4 -Co-initiated Cationic Polymerization in Open Conditions

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Abstract: The cationic polymerization of isobutylene and its block copolymerization with styrene using $\text{DiCumCl}/\text{TiCl}_4/2,6$ -lutidine initiating system has been studied in open conditions. It was shown that a higher concentration of proton trap is required in open conditions as compared to the glove box technique in order to have good control over molecular weight and polydispersity. Polyisobutylenes with $M_n \leq 50,000 \text{ g mol}^{-1}$ and low polydispersity ($\text{Đ} \leq 1.2$) were prepared at $[\text{Lu}] = 12 \text{ mM}$. The synthesis of poly(styrene-*block*-isobutylene-*block*-styrene) triblock copolymer (SIBS) in open conditions required the addition of proton trap into two steps, half at the beginning of the reaction and the second half together with styrene. Following this protocol, a series of triblock copolymers with different length of central polyisobutylene block (from $M_n = 20,000 \text{ g mol}^{-1}$ to $50,000 \text{ g mol}^{-1}$) and side polystyrene blocks ($M_n = 4000 \text{ g mol}^{-1}$ – 9000 g mol^{-1}) with low polydispersity ($\text{Đ} \leq 1.25$) were synthesized. High molecular SIBS ($M_n > 50,000 \text{ g mol}^{-1}$) with low polydispersity ($\text{Đ} < 1.3$) containing longer polystyrene blocks ($M_n > 6000 \text{ g mol}^{-1}$) demonstrated higher tensile strength ($\sim 13.5 \text{ MPa}$).

Keywords: cationic polymerization; living polymerization; isobutylene; styrene; polyisobutylene; poly(styrene-*block*-isobutylene-*block*-styrene)

1. Introduction

Poly(styrene-*block*-isobutylene-*block*-styrene) triblock copolymer (SIBS) consists of rubbery polyisobutylene block and glassy polystyrene side blocks behaves as thermoplastic elastomers similarly to poly(styrene-*block*-butadiene-*block*-styrene) or poly(styrene-*block*-isoprene-*block*-styrene) [1–3]. Besides good mechanical properties, SIBS also has the advantage of a completely saturated polyisobutylene mid-block that yields superior thermal, oxidative stability, and gas barrier properties [1–4]. Moreover, SIBS is biostable as well as bio- and hemocompatible that makes it perfect candidate for medical applications [3,5–8]. Particularly, SIBS was used as coatings on metallic stents [5,7], carrier for a drug-eluting coronary stents [5,7], ophthalmic implants [5–7], artificial vascular graft [6,9], etc. In addition, SIBS reinforced with knitted polyester fabric or carbon nanotubes is considered

as promising material for synthetic heart valve production [5,10]. Apart from biomedical applications, SIBS can be used as vibration-proof material for cars, washing machines [4], as well as for preparation of anion exchange membranes [11,12].

Typically, the synthesis of triblock copolymers of isobutylene with styrene involves the living cationic polymerization of isobutylene using difunctional initiator followed by the addition of styrene at close to complete conversion of isobutylene to generate polystyrene side blocks [13,14]. The first initiating system for the synthesis of SIBS proposed by Kennedy et al. consists of dicumyl methyl ether (DiCumOMe) as initiator and TiCl_4 as co-initiator as well as electron pair donor (N,N-dimethylacetamide) and proton trap (2,6-di-*tert*-butylpyridine, DTBP) as additives. Using this initiating system, a series of triblock copolymers with number-average molecular weight from 40,000 g mol^{-1} to 110,000 g mol^{-1} with $\bar{D} \leq 1.43$ was successfully synthesized and the best balance of properties was obtained in case of simultaneous presence of electron donor and proton trap [15]. Faust et al. showed later that living cationic polymerization of isobutylene and styrene can be achieved only in the presence of proton trap (DTBP), the only one function of which is to suppress the undesirable protic initiation [16,17]. Based on these investigations, a series of triblock copolymers with varying M_n of polyisobutylene middle block (from 39,000 g mol^{-1} to 156,000 g mol^{-1}) and polystyrene end-blocks (from 1000 g mol^{-1} to 19,000 g mol^{-1}) with very low polydispersity ($\bar{D} < 1.15$) was synthesized using *tert*-butyl dicumyl chloride/ TiCl_4 /DTBP initiating system in methylcyclohexane/ CH_3Cl (60:40 *v/v*) mixture at -80°C [18]. An exhaustive study directed to elucidation of relationship between mechanical properties and molecular weight and composition of triblock copolymers was then performed. The important observation from this study was that tensile strength of SIBS increased with increasing polystyrene content at constant PIB block length and for adequate phase separation PSt content should be in the range of 23–38 wt% [18,19]. Moreover, the phase separation in SIBS starts when molecular weight of polystyrene segment reached $\sim 5000 \text{ g mol}^{-1}$ and completed at $M_n(\text{PSt}) \sim 14,000 \text{ g mol}^{-1}$ [18]. Therefore, the tensile strength does not depend on the M_n of middle PIB block, but increases with increasing the molecular weight of polystyrene side blocks [18]. Other important recommendations regarding to the synthesis of SIBS with dicumyl chloride/ TiCl_4 /pyridine initiating system was given by Storey et al. [20]. First of all, the time of addition of styrene into living polyisobutylene chains is key issue in achieving good blocking efficiency. The addition of styrene at intermediate conversion of isobutylene results in significant retardation of polymerization due to the very low reactivity of $-\text{St}-\text{IB}-\text{Cl}$ chain ends generated due to the copolymerization of IB and St [20–23]. On the other hand, the late addition of styrene leads to contamination of block copolymer with polystyrene and polyisobutylene due to the low stability of living polyisobutylene chains under monomer-starved conditions [20,24]. It should be noted that synthesis of block copolymers of isobutylene and styrene, with very rare exceptions [25], was performed using TiCl_4 as a co-initiator, which requires using it in very high concentrations [1–4,15–24,26,27]. Another serious limitation of the known procedures of SIBS preparation is the invariable use of cumbersome glove box technique [1–4,15–24,26,27]. However, Ivan et al. reported that living cationic polymerization of isobutylene using DiCumOH/ TiCl_4 /DTBP initiating system could be successfully conducted in open air (laboratory hoods). Moreover, the possibility to synthesize well-defined triblock copolymer of IB with St under such conditions was also demonstrated using the same initiating system and mixture of proton trap and electron donor (N,N-dimethylacetamide) [28]. Although the high blocking efficiency was demonstrated by extraction of product by methylethylketone, no data about the mechanical properties of thus synthesized block copolymers were reported [28].

In this work, we report the detailed study directed to the conducting of living cationic polymerization of isobutylene and its block copolymerization with styrene using DiCumCl/ TiCl_4 /2,6-lutidine (Lu) initiating system in open conditions, i.e., without using of cumbersome glove box technique. The study of effect of proton trap concentration and mode of its addition into the system allowed to develop a simple procedure for the

synthesis of well-defined SIBS in open conditions, which consists in the addition of proton trap into two steps, half at the beginning of the reaction and the second half together with styrene. Following this protocol, a series of triblock copolymers with different length of PIB and PSt segments was synthesized and their tensile properties were estimated.

2. Materials and Methods

2.1. Materials

Isobutylene (Sigma, St. Louis, MO, USA, 99%) was dried in the gaseous state by passing through Laboratory Gas Drying Unit Drierite™ (W. A. Hammond drierite company, Ltd, Xenia, OH, USA), condensed, and stored under molecular sieves. CH₂Cl₂ (Ecos-1, Moscow, Russia, >99%) and methylcyclohexane (MCH, Merck, Darmstadt, Germany, >99%) were treated with sulphuric acid (Belreahim JSC, Minsk, Belarus, pure), washed with aqueous sodium bicarbonate (Belreahim JSC, Minsk, Belarus, pure), dried over CaCl₂ (Belreahim JSC, Minsk, Belarus, pure), refluxed, distilled twice from CaH₂ (Acros, Geel, Belgium, ca. 93%, extra pure) under inert atmosphere and stored under molecular sieves. 2,6-Dimethylpyridine (Sigma, St. Louis, MO, USA, ≥99%) and 2,6-di-*tert*-butylpyridine (Sigma, St. Louis, MO, USA, ≥97%) were dried under CaH₂ and distilled from CaH₂ under reduced pressure. TiCl₄ (Sigma, St. Louis, MO, USA, ≥99%) was distilled with copper chips under reduced pressure. Stabilized styrene (Sigma, St. Louis, MO, USA, >99%) was treated with 10% KOH (Belreahim JSC, Minsk, Belarus, pure) aqueous solution, repeatedly washed with water, dried first with CaCl₂ and then with CaH₂, and, finally, distilled two times over CaH₂ under reduced pressure. Molecular sieves (Acros, Geel, Belgium, 4 Å) were dried under reduced pressure at 200 °C for 30 min. Dicumyl alcohol (Sigma, St. Louis, MO, USA, >97%) was used as received.

Initiator, 1,4-Bis(2-chloro-2-propyl)benzene (dicumyl chloride, DiCumCl) was synthesized by passing gaseous HCl through a methylene chloride solution of 1,4-bis(2-hydroxy-2-propyl)benzene (dicumyl alcohol) at 0 °C followed by recrystallization from *n*-hexane (Ecos-1, Moscow, Russia, >99%) and drying of resulting product in vacuum [29].

2.2. Polymerization Procedures

Polymerization experiments were performed at −80 °C in three-necked flask equipped with mechanical stirrer under argon atmosphere. In a typical example of polymerization of isobutylene, the flask chilled to −80 °C was charged by 11.0 mg (48 μmol) dicumyl chloride, 18.7 mL of methylcyclohexane (MCH), 12.4 mL methylene chloride, 46 μL (0.40 mmol) of 2,6-dimethylpyridine, and 2.9 mL (34 mmol) of chilled isobutylene. The reaction mixture was agitated during 10–15 min and then the polymerization was initiated by the addition of 0.21 mL (1.9 mmol) of TiCl₄. During the polymerization process, samples were taken from reaction mixture and poured into chilled ethanol to monitor the conversion gravimetrically. The synthesis of triblock copolymer was performed in a similar manner, with the exception of the addition of 4.6 mL of 2.0 M styrene solution in a CH₂Cl₂/MCH mixture containing 23 μL (0.20 mmol) 2,6-dimethylpyridine at close to complete IB conversion (conv. = 99%, reaction time: 41 min). To quench the reaction, the excess of ethanol was added into reactor. Block copolymer was separated from reaction mixture, dried under reduced pressure. The purification of block copolymer was performed via its solubilization in *n*-hexane/CH₂Cl₂ mixture (50:50 *v/v*), filtration, and re-precipitation in high excess of ethanol. After drying under reduced pressure, the conversion of styrene was determined gravimetrically. The composition of block copolymers (content of styrene, wt%) was determined by ¹H NMR spectroscopy.

2.3. Methods

Size exclusion chromatography (SEC) was performed on an Ultimate 3000 Thermo Scientific apparatus (Thermo Fisher Scientific Dionex, Sunnyvale, CA, USA) with Agilent PLgel 5 μm MIXED-C (300 × 7.5 mm, Agilent Technologies, Santa Clara, CA, USA) column and one precolumn (PLgel 5 μm guard 50 × 7.5 mm, Agilent Technologies, Santa Clara,

CA, USA) thermostated at 30 °C. The detection was achieved by differential refractometer (RI) as well as diode array detector (UV). Tetrahydrofuran (THF, LiChrosolv®, Merck, Darmstadt, Germany, >99.9%) was eluted at a flow rate of 1.0 mL/min. The calculation of molar mass and polydispersity was carried out using EasiCal polystyrene standards (Agilent Technologies, Santa Clara, CA, USA). ^1H spectra were recorded in CDCl_3 (Euriso-top®, Gifsur Yvette, France) at 25 °C on a Bruker Avance-500 (Bruker, Billerica, MA, USA) spectrometer calibrated relative to the residual solvent resonance. The content of H_2O in the solvents and monomer was determined by a semi-micro method on an automatic titrator Titrino 848/877 (Metrohm AG, Herisau, Switzerland) using the Karl Fischer method.

Triblock copolymers of isobutylene with styrene were subjected to uniaxial tension testing using a Z-series universal testing machine (ZwickRoell AG, Ulm, Germany) equipped with a 50 N rated force sensor at 24 °C. Polymer films were cut using a custom dumbbell-shaped knife with a width of 2 mm and length of 10 mm ($n = 8$ per group). Samples were subjected to one loading cycle with a constant speed of 50 mm/min until break. Tensile strength was defined as a maximum stress (MPa) after accounting for samples' cross-sectional area. Deformation was defined as a relative elongation at maximum load.

3. Results

3.1. Polymerization of Isobutylene

3.1.1. Effect of Proton Trap Nature and Initiator Concentration

In a previous work [8], we have demonstrated that for the synthesis of triblock copolymer of isobutylene and styrene (SIBS, $M_n = 33,000 \text{ g mol}^{-1}$, $\text{Đ} = 1.30$) in open conditions (without using of glovebox), the slightly higher concentrations of TiCl_4 (59 mM vs. 40 mM [20]) and proton trap (5.8 mM vs. 3.8 mM) need to be used for providing comparable reaction rate and crossover efficiency during block copolymer preparation. This could be explained by a much higher amount of adventitious H_2O in the system when the preparation of block copolymer is performed in open conditions as compared to the glovebox technique. Although the Karl Fischer titration gives 1.6 mM of H_2O in solvents and monomer in our conditions that is comparable to the content of H_2O in reactants stored in glovebox 1–1.5 mM [30,31], an additional H_2O may be brought into reactor in the course of its charging by solvents and monomer performed in open conditions.

In order to make the initiating system cheaper, we substituted expensive 2,6-di-*tert*-butylpyridine (DTBP) by 2,6-dimethylpyridine (2,6-lutidine, Lu). As it is evident from Figure 1a, the first-order plots are linear for both proton traps investigated giving almost similar values of apparent rate constant of propagation: $k_{p, \text{app}} = 1.80 \times 10^{-1} \text{ min}^{-1}$ and $1.71 \times 10^{-1} \text{ min}^{-1}$ for DTBP and Lu, respectively. In addition, experimental values of M_n are correlated well with theoretical line, while polydispersity decreases with increasing monomer conversion reaching of values of 1.2 at close to complete monomer conversion for both proton traps investigated (Figure 1b). Therefore, the cationic polymerization of IB proceeds in a living fashion with both $\text{DiCumCl}/\text{TiCl}_4/\text{DTBP}$ and $\text{DiCumCl}/\text{TiCl}_4/\text{Lu}$ initiating systems and DTBP could be successfully replaced by much cheaper Lu.

Aiming at defining the potential of $\text{DiCumCl}/\text{TiCl}_4/\text{Lu}$ initiating system in the synthesis of well-defined high molecular weight polyisobutylene, the polymerization experiments were carried out at different initiator concentrations. As anticipated, the reaction rate gradually decreased with decreasing the concentration of initiator, on the one hand (Figure 1a). On the other hand, the first-order plots are linear for all initiator concentrations studied (Figure 1a) indicating the absence of irreversible termination. The number-average molecular weight increased with increasing isobutylene conversion, while experimental values of M_n are inversely proportional to concentration of initiator. Although perfect correlation between experimental M_n s and theoretical values was achieved for DiCumCl concentration of 2.8 mM, some deviation from theoretical line was observed for $[\text{DiCumCl}] = 1.4 \text{ mM}$. Moreover, a significant deviation of experimental values of M_n from a theoretical line was found for the lowest initiator concentration studied (Figure 1b). In addition, polydispersity

is higher for experiments performed at DiCumCl concentration of 1.4 and 1.1 mM as compared to polymerization with higher initiator concentration (Figure 1b).

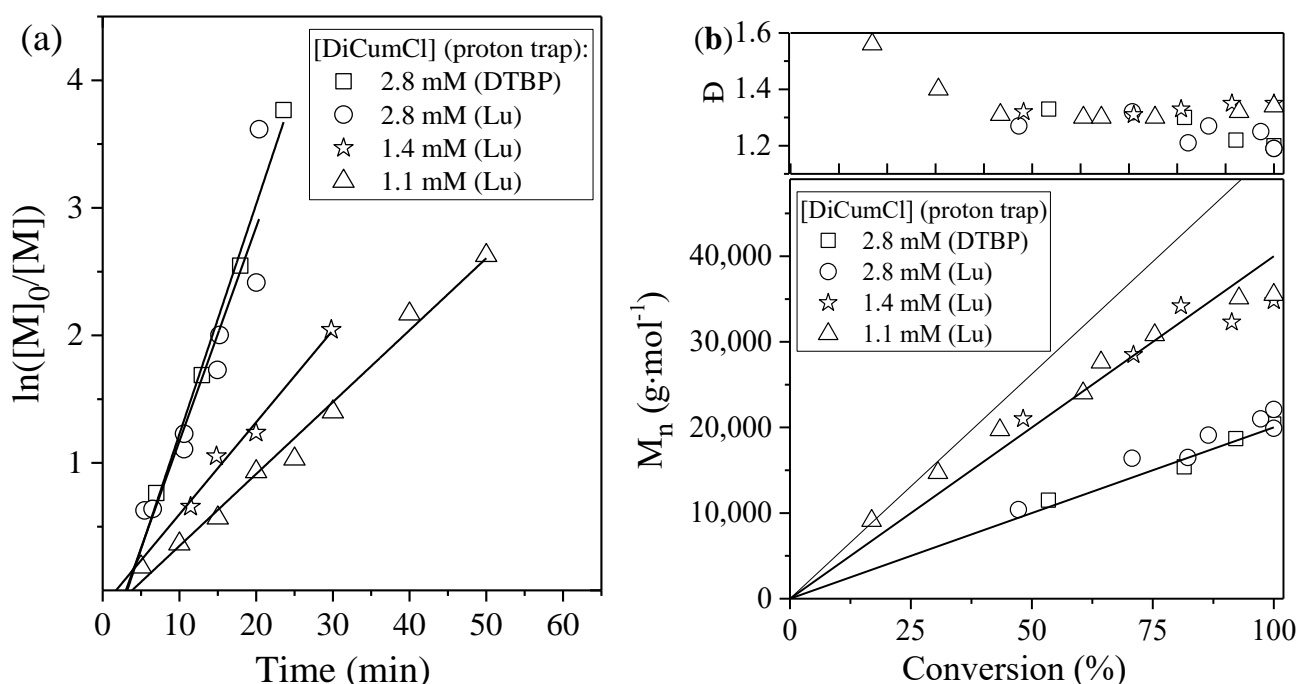


Figure 1. (a) First-order plots and (b) M_n , \bar{D} vs. conversion dependences for cationic polymerization of isobutylene at with DiCumCl/TiCl₄/proton trap initiating system in CH₂Cl₂/MCH 40:60 *v/v* at different initiator concentrations at -80°C : [IB] = 1.0 M; [TiCl₄] = 59 mM; [DTBP] = [Lu] = 5.8 mM.

This deviation may be attributed to the competitive initiation of polymerization via adventitious H₂O, which becomes visible at low initiator concentration. To check this point, ¹H NMR spectra of polymers prepared at [DiCumCl] = 2.8 mM and 1.1 mM at close to complete monomer conversions were analyzed (Figure 2a). According to Figure 2a, polyisobutylene ($M_{n, \text{SEC}} = 19,900 \text{ g mol}^{-1}$, $\bar{D} = 1.19$; conv. = 99%) obtained at [DiCumCl] = 2.8 mM is characterized by high end group fidelity (only chlorine end groups) as well as quantitative incorporation of difunctional initiator into the polymer chain: no monofunctional PIB chains generated due to the initiation by adventitious H₂O was detected. Indeed, the number-average molecular weights calculated from ¹H NMR spectrum based on the signals of fragment of initiator ($M_{n, \text{NMR}}(\text{DiCum}) = 20,400 \text{ g mol}^{-1}$) and chlorine end group ($M_{n, \text{NMR}}(\text{Cl}) = 20,100 \text{ g mol}^{-1}$) are almost identical and close to M_n determined by SEC. In strong contrast, for PIB synthesized at [DiCumCl] = 1.1 mM, the number-average molecular weight calculated from ¹H NMR spectrum ($M_{n, \text{NMR}}(\text{DiCum}) = 62,400 \text{ g mol}^{-1}$) is much higher than one obtained by SEC ($M_n(\text{SEC}) = 35,500 \text{ g mol}^{-1}$) confirming that protic initiation via adventitious H₂O is indeed significant at low initiator concentration under investigated conditions.

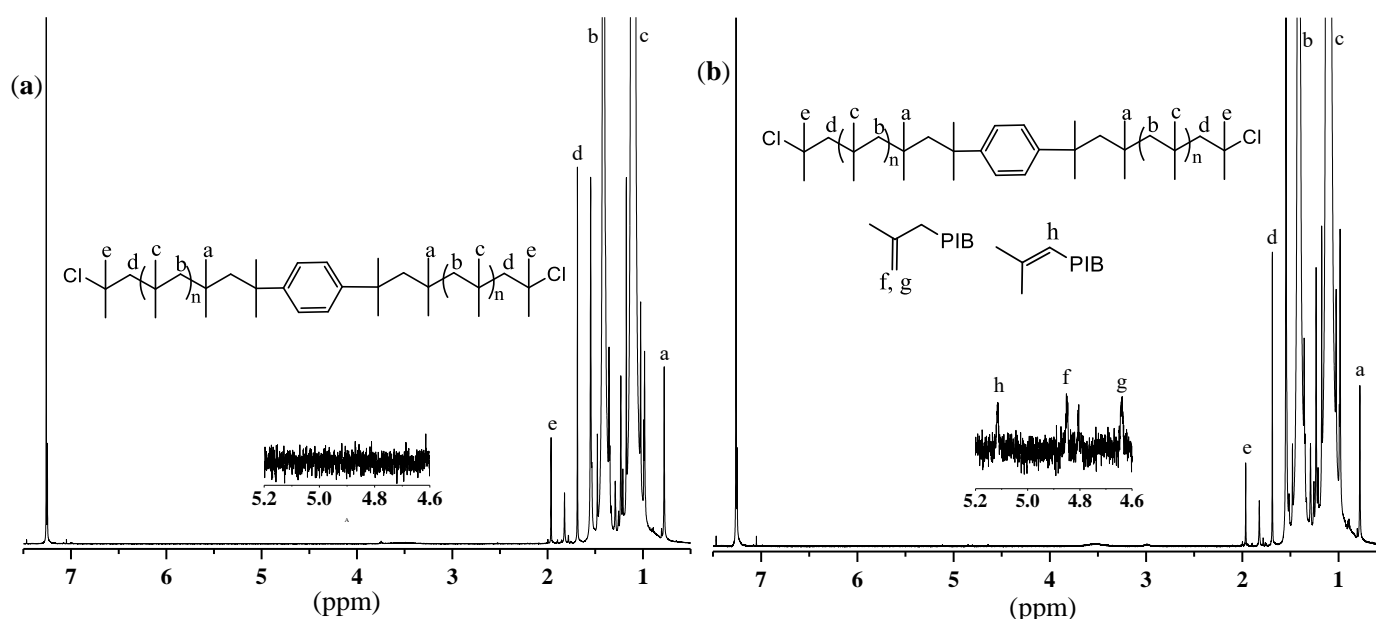


Figure 2. ^1H NMR spectrum of PIB prepared with $\text{DiCumCl}/\text{TiCl}_4/\text{Lu}$ initiating system (a) at high initiator concentration ($[\text{DiCumCl}] = 2.8 \text{ mM}$; $[\text{Lu}] = 5.8 \text{ mM}$) and (b) at high concentration of proton trap ($[\text{DiCumCl}] = 1.4 \text{ mM}$; $[\text{Lu}] = 23.4 \text{ mM}$).

3.1.2. Effect of Proton Trap Concentration

To find optimal concentration of proton trap for complete suppression of undesirable initiation via H_2O , the effect of proton trap concentration on the reaction rate as well as properties of the synthesized polyisobutylenes has been investigated. As it was anticipated, the addition of 5.8 mM of proton trap into the system results in significant decrease of reaction rate ($k_{p, \text{app}} = 16.9 \times 10^{-2} \text{ min}^{-1}$ and $7.2 \times 10^{-2} \text{ min}^{-1}$ for $[\text{Lu}] = 0 \text{ mM}$ and 5.8 mM, respectively). The further increase of proton trap concentration from 5.8 mM to 17.5 mM almost does not influence the reaction rate ($k_{p, \text{app}} = 7.2 \times 10^{-2} \text{ min}^{-1}$ and $7.9 \times 10^{-2} \text{ min}^{-1}$) indicating the absence of complexation of TiCl_4 with Lu, while the formation of complex between 2,4-dimethylpyridine and TiCl_4 was reported by Storey et al. [31,32]. However, some retardation of reaction was observed at highest Lu concentration ($k_{p, \text{app}} = 5.0 \times 10^{-2} \text{ min}^{-1}$ at $[\text{Lu}] = 23.4 \text{ mM}$). This observation is consistent with the known possibility of hindered pyridines such, for example, DTBP to abstract protons from β -H position to growing macrocation [33–35]. This process is typically became visibly under monomer-starved conditions [34], while it may also occur in the course of reaction at high proton trap concentration [35].

Indeed, a close inspection of M_n vs. conversion plots revealed the deviation of experimental values of the number-average molecular weight from theoretical line for experiments performed at high concentration of proton trap ($[\text{Lu}] \geq 17.5 \text{ mM}$) (Figure 3b). This indicates that proton trap may act as a chain transfer agent when it used at relatively high concentration that is also confirmed by ^1H NMR spectroscopy by the appearance of signals corresponding to olefin end groups (Figure 2b). Indeed, strong bases could regioselectively abstract protons in β -position toward growing macrocations [34,36]. On the other hand, the same deviation from theoretical line is observed at $[\text{Lu}] = 5.8 \text{ mM}$ (Figure 3b) indicating that protic initiation via adventitious H_2O is not fully suppressed at such conditions. In fact, polydispersity is relatively high ($M_w/M_n = 1.35\text{--}1.40$) at $[\text{Lu}] \leq 5.8 \text{ mM}$ decreasing down to $M_w/M_n \leq 1.2$ at $[\text{Lu}] \geq 11.7 \text{ mM}$. It should be also noted that good correlation between the number-average molecular weight determined by SEC ($M_n = 51,800 \text{ g mol}^{-1}$) and ^1H NMR spectroscopy ($M_{n, \text{NMR}}(\text{DiCum}) = 54,600 \text{ g mol}^{-1}$) was observed for $[\text{Lu}] \geq 11.7 \text{ mM}$ in case of using lowest concentration of initiator ($[\text{DiCumCl}] = 1.1 \text{ mM}$).

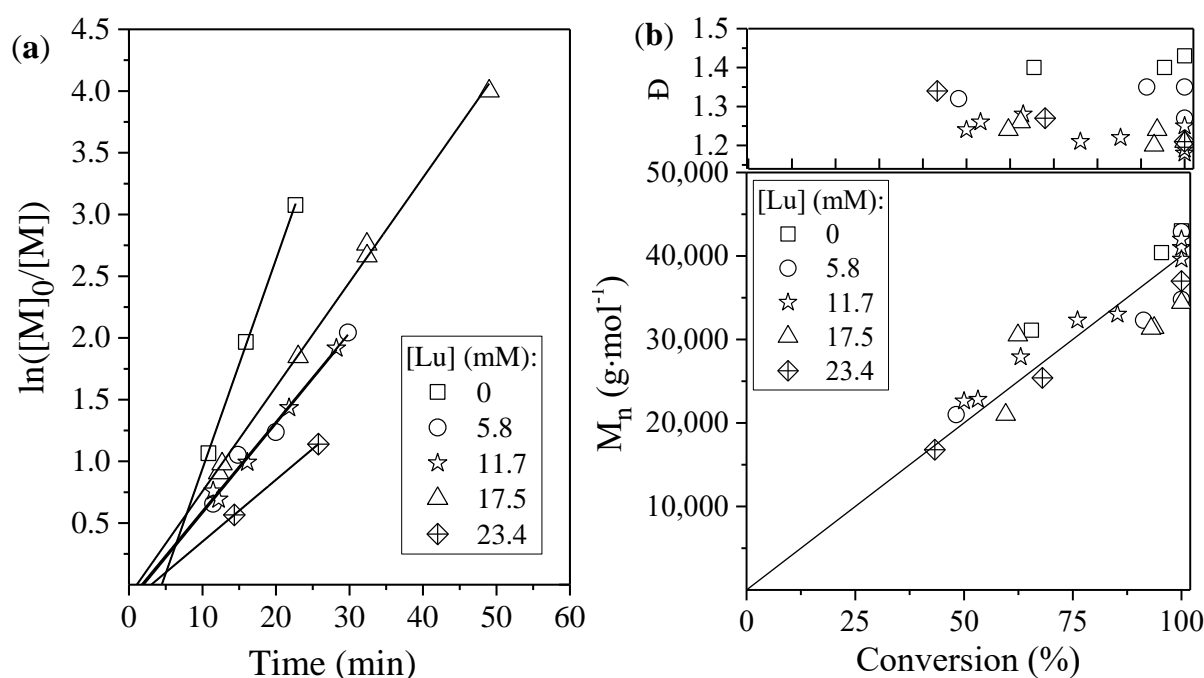


Figure 3. (a) First-order plots and (b) M_n , \bar{D} vs. conversion dependences for cationic polymerization of isobutylene at with DiCumCl/TiCl₄/Lu initiating system in CH₂Cl₂/MCH 40:60 v/v at different proton trap concentrations at -80°C : [IB] = 1.0 M; [TiCl₄] = 59 mM; [DiCumCl] = 1.4 mM.

To summarize, the optimal concentration of proton traps is about 12 mM when polymerization is performed in open conditions. At this concentration of proton trap the good correlation between experimental (determined by both SEC and ^1H NMR) and theoretical molecular weights is observed for DiCumCl of 1.4 mM (Figure 3b) and 1.1 mM (Figure S1), while polydispersity does not exceed 1.2. In addition, at this proton trap concentration, the synthesized PIBs are characterized by high end group fidelity (only chlorine end groups) as well as quantitative incorporation of difunctional initiator into the polymer chain. It should be also noted that effective concentration of proton trap is about seven times higher than concentration of H₂O in reactants that implies that significant amount of H₂O may penetrate into the system in course of reactants and, especially, cooled isobutylene dosage.

3.2. Synthesis of Triblock Copolymers

The next step of our research program was the synthesis of triblock copolymers of isobutylene and styrene (SIBS) in open conditions via consecutive living cationic polymerization of isobutylene with difunctional initiator followed by the polymerization of styrene using optimal conditions developed for homopolymerization of IB (vide supra). In line with our previous results, an attempt to prepare triblock copolymer without an addition of proton trap or using low concentrations of Lu results in product with broad or even bimodal molecular weight distribution (runs 3, 4 in Table 1 and Figure S2a,b). The comparison of SEC traces recorded with RI and UV detectors revealed the presence of significant fraction of homopolystyrene in product (Figure S2a,b), which is most probably generated via protic initiation. At optimal for homopolymerization of IB concentration of proton trap (11.7 mM), triblock copolymers were successfully prepared; however, a small fraction of homopolystyrene is still presented that result in broadening of molecular weight distribution (run 5 Table 1). Similarly to homopolymerization of IB (Figure 3a), the further increase of proton trap concentration does not improve the properties of triblock copolymer (runs 5, 6, Table 1, Figure 4a). However, a significant amount of adventitious H₂O could penetrate into reactor in the course of cooled styrene addition via pipette. Therefore, taking into account that excessive free proton trap may act as a chain transfer agent (vide

supra), the idea was to introduce the proton trap into two steps, half at the beginning of the reaction and the second half together with styrene. This approach would allow keeping the concentration of free proton trap at relatively low level to suppress undesirable β -H abstraction, on the one hand. On the other hand, the addition of proton trap into two steps would allow maintaining its concentration higher than the concentration of adventitious H_2O .

Table 1. Synthesis of triblock copolymers of isobutylene with styrene (SIBS) using DiCumCl/TiCl₄/Lu initiating system ¹.

| Run | [DiCumCl] (mM) | [Lu ₁] ² (mM) | [Lu ₂] ² (mM) | $M_{n, \text{theor}}$ ³ (g mol ⁻¹) | M_n (PIB) (g mol ⁻¹) | \bar{D} | $M_{n, \text{theor}}$ ⁴ (g mol ⁻¹) | M_n (SIBS) (g mol ⁻¹) | \bar{D} |
|-----------------|-------------------|---|---|--|---------------------------------------|-----------|--|--|-----------|
| 1 | 2.8 | 5.8 | 0 | 20,230 | 21,400 | 1.23 | 30,230 | 24,900 | 1.37 |
| 2 | 2.8 | 5.8 | 5.8 | 20,230 | 21,100 | 1.17 | 30,230 | 29,400 | 1.21 |
| 3 | 1.4 | 0 | 0 | 40,230 | 43,000 | 1.43 | 60,230 | 25,000 | 2.62 |
| 4 | 1.4 | 5.8 | 0 | 40,230 | 40,500 | 1.33 | 60,230 | 33,200 | 1.86 |
| 5 | 1.4 | 11.7 | 0 | 40,230 | 41,000 | 1.25 | 60,230 | 43,200 | 1.46 |
| 6 | 1.4 | 17.5 | 0 | 40,230 | 45,100 | 1.38 | 60,230 | 42,700 | 1.46 |
| 7 | 1.4 | 11.7 | 5.8 | 40,230 | 42,000 | 1.18 | 60,230 | 49,700 | 1.23 |
| 8 | 1.4 | 11.7 | 11.7 | 40,230 | 39,600 | 1.19 | 60,230 | 45,800 | 1.21 |
| 9 ⁵ | 1.1 | 5.8 | 5.8 | 52,730 | 41,300 | 1.27 | 75,230 | 59,300 | 1.62 |
| 10 ⁵ | 1.1 | 11.7 | 11.7 | 52,730 | 51,800 | 1.21 | 75,230 | 64,200 | 1.28 |

¹ Conditions: [IB] = 1.0 M; [St] = 0.27 M; [TiCl₄] = 59 mM; CH₂Cl₂/MCH 40:60 v/v; −80 °C. ² Lu₁ and Lu₂ are concentrations of proton trap added before introduction of IB and together with styrene, respectively. ³ $M_{n, \text{theor}}(\text{PIB}) = [\text{IB}]/[\text{DiCumCl}] \times \text{conv.}(\text{IB}) + M_r(\text{DiCumCl})$.

⁴ $M_{n, \text{theor}}(\text{SIBS}) = [\text{IB}]/[\text{DiCumCl}] \times \text{conv.}(\text{IB}) + [\text{St}]/[\text{DiCumCl}] \times \text{conv.}(\text{St}) + M_r(\text{DiCumCl})$. ⁵ [TiCl₄] = 90 mM; [St] = 0.23 M.

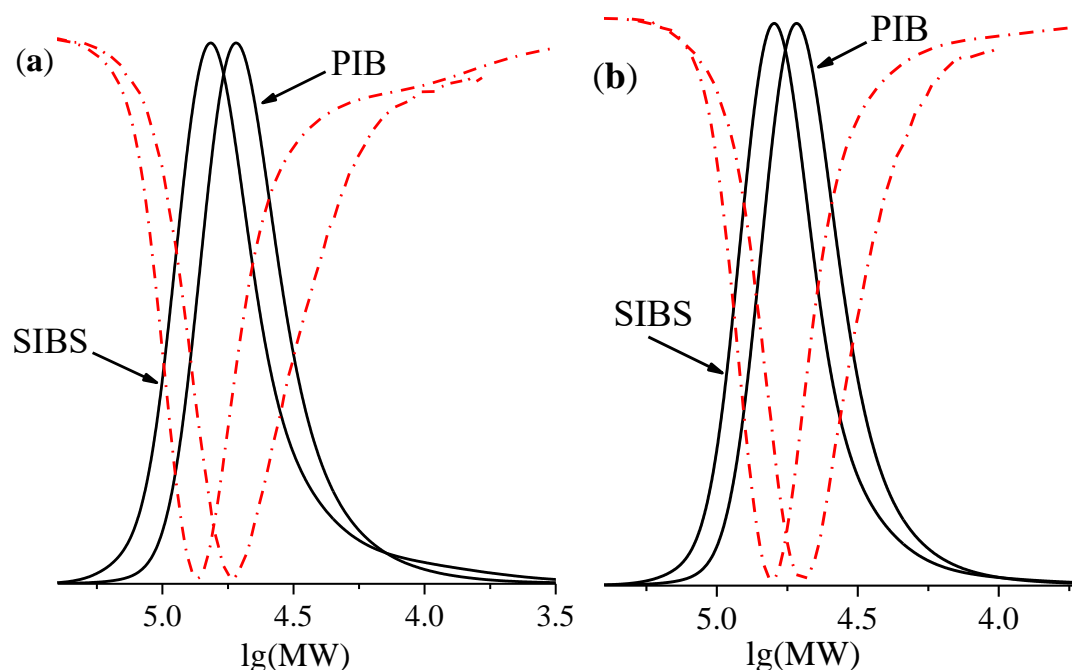


Figure 4. RI (solid line) and UV (dashed line) SEC traces of polyisobutylenes and corresponding SIBSs obtained with DiCumCl/TiCl₄/Lu initiating system in CH₂Cl₂/MCH 40:60 v/v at −80 °C using different modes of proton trap addition. Proton trap addition: (a) one-step (run 6, Table 1); (b) two-steps (run 7, Table 1).

Indeed, the addition of proton traps into two steps results in significant improvement of polydispersity of synthesized triblock copolymers as well as reduction of the fraction of homopolystyrene (compare runs 6 and 7, Table 1, Figure 4b). The higher concentration of proton trap is required in each step for the synthesis of SIBS with higher molecular weight (runs 9, 10 in Table 1). Oppositely, the lower concentration of proton trap will be enough for the preparation of triblock copolymer of lower molecular weight (runs 1, 2

in Table 1). In summary, using two-step addition of proton trap, well-defined triblock copolymers of styrene with different length of central polyisobutylene block (from $M_n = 20,000 \text{ g mol}^{-1}$ to $50,000 \text{ g mol}^{-1}$) with low polydispersity ($\text{Đ} \leq 1.25$) were successfully prepared in open conditions.

Another important aspect of the synthesis of triblock copolymers of isobutylene and styrene, which may influence the properties of final product, is the time of polymerization of styrene. As it can be seen from Figure 5a, the addition of St to living polyisobutylene macrocations leads to shift of SEC curve into high molecular weight region indicating that polymerization of styrene proceeds in a living fashion. However, a small shoulder appeared in the high molecular weight region at complete monomer conversion. The reason for that may be intermolecular alkylation during the formation of polystyrene block under monomer-starved conditions. To confirm this assumption, the triblock copolymer was kept under monomer-starved conditions for 1 h. The continuous increase of content of high molecular weight fraction with its simultaneous shift into high molecular weight region confirms this assumption (Figure 5b). Similar formation of shoulder in high molecular weight region of SEC tracers was observed by Puskas et al. in the course of preparation of SIBS [4].

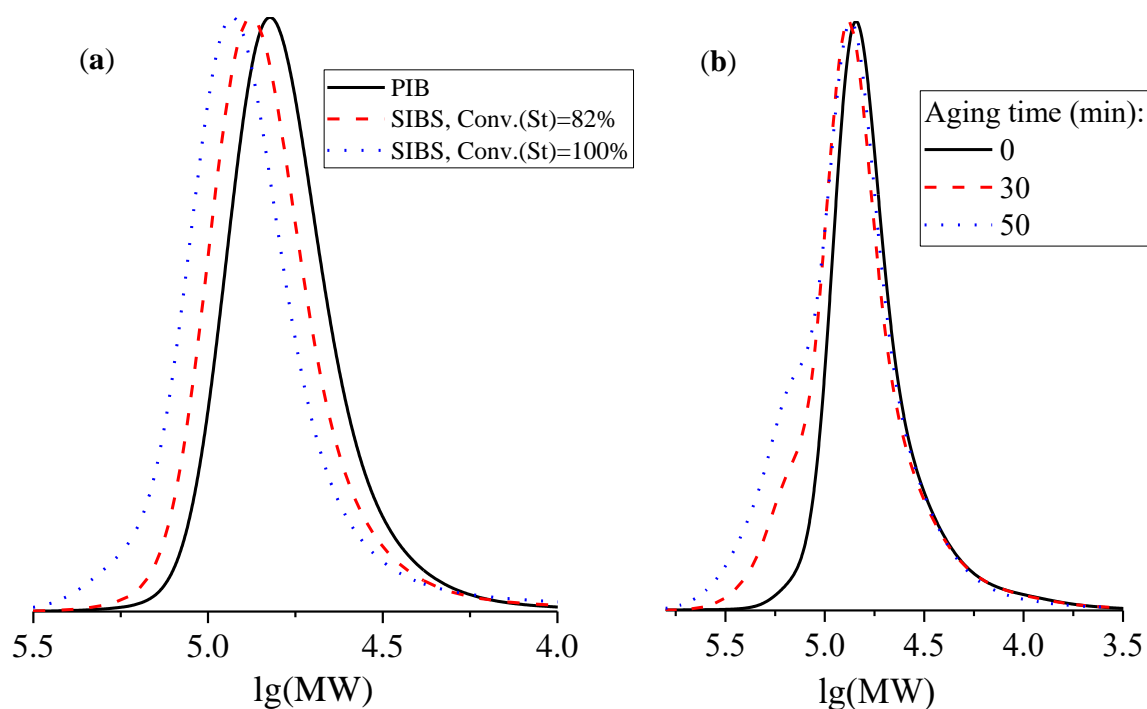


Figure 5. (a) SEC traces for the preparation of SIBS at different styrene conversions (run 10, Table 1); (b) evolution of SEC traces of SIBS with time at complete monomer conversion.

3.3. Mechanical Properties

The triblock copolymer with different lengths of polyisobutylene middle block and polystyrene side block synthesized under open conditions were subjected to uniaxial tension testing (Table 2). According to data presented in Table 2, for acceptable mechanical properties the molecular weight of polyisobutylene block should be higher than $35,000 \text{ g mol}^{-1}$. Indeed, both tensile strength and elongation at break are significantly increased with increasing the molecular weight of PIB block from $M_n = 21,000 \text{ g mol}^{-1}$ to $M_n = 35,000 \text{ g mol}^{-1}$, and then ($M_n(\text{PIB}) = 45,000 \text{ g mol}^{-1}$) almost do not change (runs 1–3 in Table 2). The tensile strength gradually increased from 6.03 MPa to 13.26 MPa with increasing the molecular weight of polystyrene side block from $M_n = 4600 \text{ g mol}^{-1}$ to 9000 g mol^{-1} , respectively, but less depended on the content of styrene in a copolymer (runs 3–5, Table 2) that is consistent with the earlier reports [4,15,18]. In addition, SIBSs

with lower polydispersity displayed better tensile strength even at shorter polystyrene side block (runs 4, 5 in Table 2) that emphasizes the high importance of the preparation of well-defined block copolymers. The typical stress-strain curves for block copolymers with different polystyrene block length can be seen in Figure 6.

Table 2. Tensile properties of SIBS triblock copolymers of different composition at 24 °C.

| Run | M_n (SIBS) (g mol ⁻¹) | \bar{D} | M_n (PSt) ¹ (g mol ⁻¹) | St ² (wt%) | Tensile Strength (MPa) | Elongation at Break (%) |
|-----|--|-----------|--|--------------------------|---------------------------|----------------------------|
| 1 | 33,000 | 1.30 | 6000 | 29 | 3.58 | 240 |
| 2 | 47,200 | 1.25 | 5700 | 29 | 6.93 | 800 |
| 3 | 54,800 | 1.40 | 4600 | 27 | 6.07 | 1140 |
| 4 | 64,200 | 1.28 | 6200 | 25 | 13.56 | 1180 |
| 5 | 59,300 | 1.62 | 9000 | 29 | 12.57 | 1470 |

¹ The number-average molecular weight of one polystyrene block. ² Determined by ¹H NMR spectroscopy.

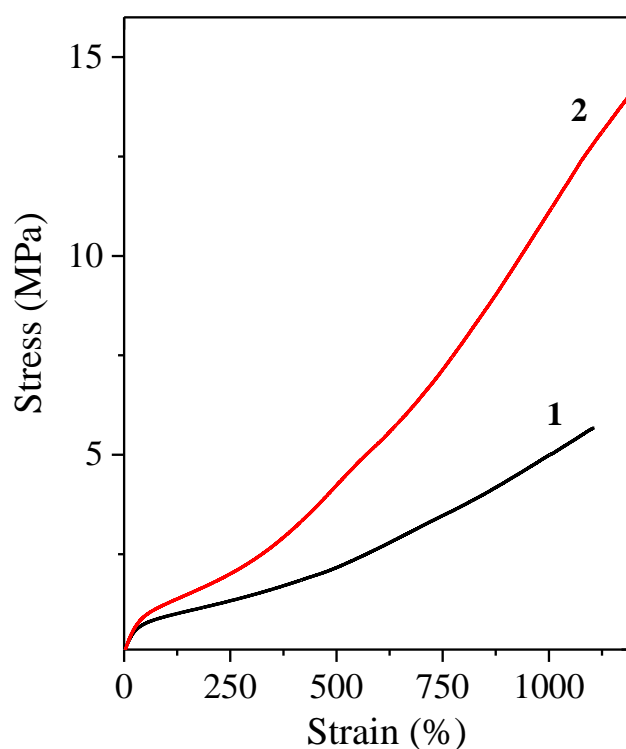


Figure 6. Typical stress-strain curves of poly(styrene-*block*-isobutylene-*block*-styrene) synthesized in this work: 1 (run 3, Table 2); 2 (run 4, Table 2).

It should be noted that the values of tensile strength of SIBS synthesized in open conditions correlated well with those for SIBS prepared using glove box technique at the similar polystyrene block lengths [4,15,18]. These data confirm the possibility to prepare well-defined poly(styrene-*block*-isobutylene-*block*-styrene) triblock copolymers using convenient laboratory conditions.

4. Conclusions

In this work, the detailed study directed to the conducting of living cationic polymerization of isobutylene and its block copolymerization with styrene using DiCumCl/TiCl₄/2,6-lutidine initiating system in open conditions, i.e., without using of cumbersome glove box technique, was reported. It was shown that although the level of adventitious water in reactants is relatively low (1.6 mM) and comparable with one reported earlier [30,31], most

of the water penetrated into the system in the course of the transfer of reagents. Therefore, higher concentration of proton trap is required to suppress initiation by adventitious H₂O in open conditions in comparison with glove box technique. We also demonstrated here that proton trap may act as a chain transfer agent abstracting protons in β -position toward growing cations when it used at relatively high concentration. Based on these findings, the simple procedure for the synthesis of well-defined SIBS in open conditions was developed, which consists in the addition of proton trap into two steps, half at the beginning of the reaction and the second half together with styrene. Following this protocol, a series of tri-block copolymers with different length of PIB and PSt segments was synthesized and their tensile properties were estimated to be comparable to those obtained for SIBS prepared using glove box technique.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/macromol1040017/s1>, Figure S1: Figure S1: (a) First-order plots and (b) M_n , \bar{D} vs. conversion dependences for cationic polymerization of isobutylene at with DiCumCl/TiCl₄/Lu initiating system in CH₂Cl₂/MCH 40:60 v/v at different proton trap concentrations at -80°C : [IB] = 1.0 M; [TiCl₄] = 90 mM; [DiCumCl] = 1.1 mM. Figure S2: RI (solid line) an UV (dot line) SEC traces of polyisobutylenes and corresponding SIBSs obtained with DiCumCl/TiCl₄/Lu initiating system in CH₂Cl₂/MCH 40:60 v/v at -80°C and at different concentration of proton trap. Concentration of proton trap: (a) 0 mM (run 3, Table 1); (b) 5.8 mM (run 4, Table 1).

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