



POLYDIETHYLSILOXANE MACROINITIATORS FOR THE SYNTHESIS OF BLOCK COPOLYMERS

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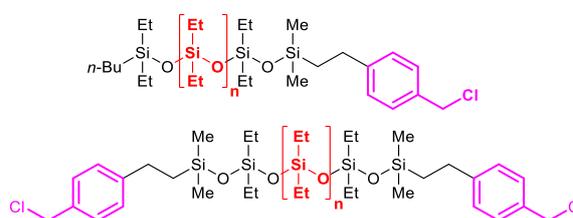
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Abstract

α -Butyl- ω -(lithiumoxy)oligodiethylsiloxane and α,ω -dipotassiumoxypolydiethylsiloxane are synthesized by the anionic polymerization of hexaethylcyclotrisiloxane in the presence of *n*-BuLi or KOH, respectively. The mono- and bifunctional polydiethylsiloxane macroinitiators are derived from the reactions of α -butyl- ω -(lithiumoxy)oligodiethylsiloxane and α,ω -dipotassiumoxypolydiethylsiloxane with chloro(dimethyl)-(4-chloromethylphenylethyl)silane. The resulting polydiethylsiloxane macroinitiators can be used for the synthesis of di- and triblock copolymers.

Key words: polydiethylsiloxane, anionic polymerization, macroinitiators, block copolymers.

Polydiethylsiloxane macroinitiators



Introduction

The controlled radical polymerization substantially expanded opportunities for regulating the structures of polymers and consequently their properties [1]. The application of macromonomers offers new possibilities for the investigation of structure–property relationships in the chemistry of block copolymers; in particular, it greatly facilitates the modification of polymer properties because macromolecules enable the targeted combination of sections of polymers which differ in the structures and properties. For example, the combination of rigid and flexible blocks of macromolecules ensures the production of modified elastomers that possess improved strength characteristics while maintaining flexibility. Many synthetic routes to block copolymers are based on two main principles: the interaction of a macroinitiator with a monomer and the interaction of two and more polymer blocks or macroradicals with each other. Owing to the propensity of block copolymers for microphase ordering, they can be used for the production of nanostructured materials [2–5].

Usually siloxane blocks play the role of soft blocks. For example, a large number of reports are devoted to the synthesis of block copolymers of polydimethylsiloxane (PDMS) and polystyrene (PS) [6,7]. These block copolymers tend to microphase separation into domains of glassy polystyrene and rubber [3, 8]. The ordered structures formed in block copolymer systems attract continuous research interest owing to the multiple options for controlling the processes of their self-organization *via* modification of molecular parameters of rigid and soft blocks [9].

Another possibility for the creation of ordered microphase

formations is realized owing to the introduction of a block with mesogenic groups. The opportunities of their ordering are determined by the presence of flexible spacers that connect the mesogenic groups with a polymer matrix [10]. The third type of ordering, which is typical for flexible chain polymers with chemical structures deprived of mesogenic groups, is less popular. These polymers can form thermodynamically stable thermotropic ordered phases, which fall in between crystalline and amorphous phases. For the first time, these mesophases were revealed in the polymers with inorganic main chains, such as polyphosphazenes [11] and polyorganosiloxanes [12–15]. The latter, bearing alkyl substituents larger than methyl, refer to the group of nonpolar flexible macromolecules, which are capable of forming column mesophases [12, 16–18], and are of particular interest for the application in block copolymers since they offer additional opportunities for the formation of ordered regions without violating a linear character of the block copolymer.

Polydiethylsiloxane (PDES) with the molar mass of 30000 g/mol and more is known to form a mesophase at the ambient temperature [12, 19]. Therefore, the block copolymers of PDES and PS can be separated into polystyrene domains, which feature mechanical strength and optical isotropy, and mesomorphous PDES domains, which demonstrate plasticity and double refraction of rays [20, 21]. Even at present, the regulation of molecular characteristics of these copolymers is scarcely explored. This is connected mainly with the absence of data on the synthesis of macroinitiators based on the PDES block. The problem is that the block copolymers of PDES and PS were sequentially obtained by the anionic polymerization of styrene and, then, the resulting macroinitiator was used for ring-

opening polymerization of hexaethylcyclotrisiloxane. The reverse order in this pair of monomers is simply impossible. This means that the potential of synthesis of block copolymers featuring the central polydiethylsiloxane block is almost unfeasible within this concept.

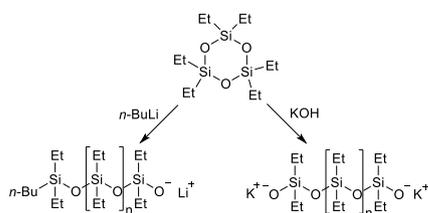
Herein, we report on the synthesis of polydiethylsiloxane macroinitiators that can be used for the production of di- and triblock copolymers of polydiethylsiloxane (B) and polystyrene (A) of AB and ABA types and, thus, can remove the restrictions in the design of block copolymer systems for this promising pair of monomers.

Results and discussion

The polydiethylsiloxane initiators, namely, α -butyl- ω -[(4-chloromethylphenylethyl)dimethylsiloxy]oligodiethylsiloxane with the calculated number of units equal to seven (based on the NMR spectroscopic data) and high-molecular α,ω -bis-[(4-chloromethylphenylethyl)dimethylsiloxy]polydiethylsiloxane were obtained by the reactions of chloro(dimethyl)-(4-chloromethylphenylethyl)silane with α -butyl- ω -(lithiumoxy)oligodiethylsiloxane or α,ω -dipotassiumoxypolydiethylsiloxane, respectively.

Synthesis of α -butyl- ω -(lithiumoxy)oligodiethylsiloxane and α,ω -dipotassiumoxypolydiethylsiloxane

α -Butyl- ω -(lithiumoxy)oligodiethylsiloxane and α,ω -dipotassiumoxypolydiethylsiloxane were obtained by the anionic polymerization of hexaethylcyclotrisiloxane in the presence of *n*-BuLi and KOH, respectively (Scheme 1).



Scheme 1. Synthesis of α -butyl- ω -(lithiumoxy)oligodiethylsiloxane and α,ω -dipotassiumoxypolydiethylsiloxane.

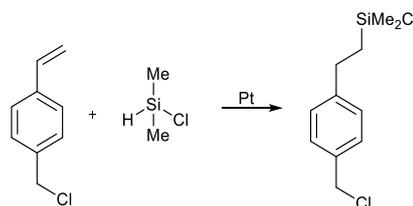
In the case of α -butyl- ω -(lithiumoxy)oligodiethylsiloxane, the anionic polymerization was carried out in an inert atmosphere (M. Braun Inertgas-Systeme GmbH) in dry toluene. The initiation of active centers was performed at room temperature under the action of *n*-BuLi. In 24 h after the formation of the active centers, DMF was added to the reaction mixture as an activator of the anionic polymerization. The chain growth was carried out at 60 °C for 8 h.

During the synthesis of α,ω -dipotassiumoxypolydiethylsiloxane, the anionic polymerization was carried out in block. KOH was chosen as an initiator. The duration of the anionic polymerization composed 1 h at 150 °C.

Synthesis of chloro(dimethyl)-(4-chloromethylphenylethyl)silane

To obtain mono- and bifunctional polydiethylsiloxane initiators, chloro(dimethyl)-(4-chloromethylphenylethyl)silane

blocking agent was synthesized for treatment of living polymers. It was obtained by the hydrosilylation of 4-vinylbenzyl chloride with dimethylchlorosilane in toluene in the presence of a platinum catalyst (Scheme 2).



Scheme 2. Synthesis of chloro(dimethyl)-(4-chloromethylphenylethyl)silane.

The conversion was controlled by ^1H NMR spectroscopy using the signals of vinyl protons. After reaching 100% conversion, the vacuum distillation of the resulting mixture afforded a fraction that contained 96% of target chloro(dimethyl)-(4-chloromethylphenylethyl)silane according to the data of gas-liquid chromatography.

The chemical structure of the resulting compound was confirmed by the ^1H NMR spectroscopic data (Fig. 1).

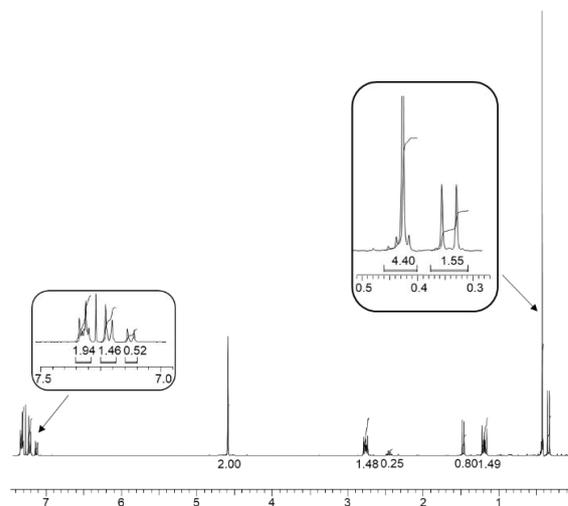
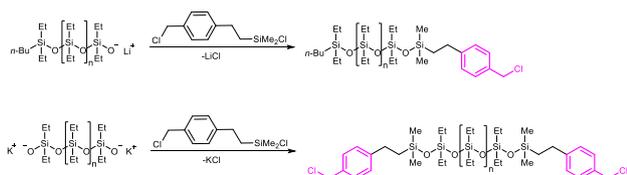


Figure 1. ^1H NMR spectrum of chloro(dimethyl)-(4-chloromethylphenylethyl)silane.

Synthesis of the polydiethylsiloxane initiators— α -butyl- ω -[(4-chloromethylphenylethyl)dimethylsiloxy]oligodiethylsiloxane and α,ω -bis-[(4-chloromethylphenylethyl)dimethylsiloxy]polydiethylsiloxane

α -Butyl- ω -[(4-chloromethylphenylethyl)dimethylsiloxy]-oligodiethylsiloxane and α,ω -bis-[(4-chloromethylphenylethyl)dimethylsiloxy]polydiethylsiloxane were synthesized according to the scheme presented below by the interaction of chloro(dimethyl)-(4-chloromethylphenylethyl)silane with α -butyl- ω -(lithiumoxy)oligodiethylsiloxane or α,ω -dipotassiumoxypolydiethylsiloxane at the reduced temperature (Scheme 3).

According to the results of the GPC analysis, the macromonomers with the following characteristics were obtained: α -butyl- ω -[(4-chloromethylphenylethyl)dimethylsiloxy]oligodiethylsiloxane with $M_n = 1350$ and polydispersity



Scheme 3. Syntheses of the mono- and bifunctional polydiethylsiloxane initiators.

index $M_w/M_n = 1.15$ and α,ω -bis-[(4-chloromethylphenylethyl)dimethylsiloxy]polydiethylsiloxane with $M_n = 85500$ and polydispersity index $M_w/M_n = 1.31$ (a fraction isolated on a preparative chromatograph) (Fig. 2).

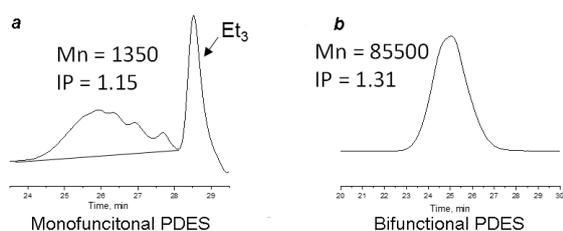


Figure 2. GPC curves: (a) α -butyl- ω -[(4-chloromethylphenylethyl)dimethylsiloxy]oligodiethylsiloxane (monofunctional PDES), here Et₃ refers to the peak of starting hexaethylcyclotrisiloxane; (b) α,ω -bis-[(4-chloromethylphenylethyl)dimethylsiloxy]polydiethylsiloxane (bifunctional PDES).

The chemical structures of the resulting macroinitiators were confirmed by the ¹H NMR spectroscopic data (Figs. 3 and 4).

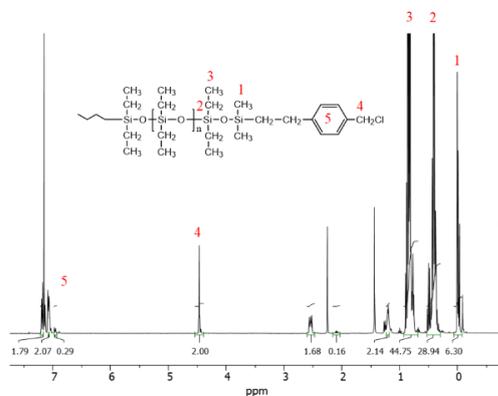


Figure 3. ¹H NMR spectrum of the resulting monofunctional macroinitiator.

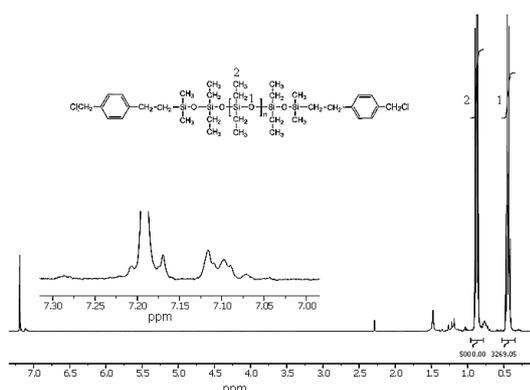
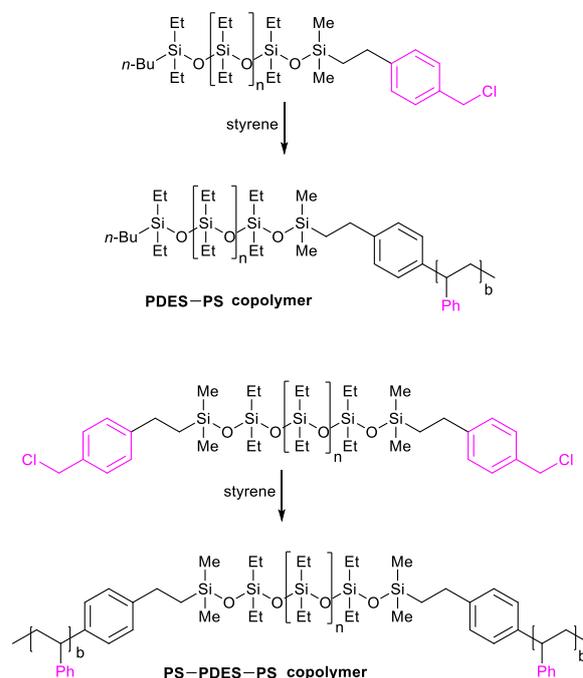


Figure 4. ¹H NMR of the resulting bifunctional macroinitiator.

The resulting mono- and bifunctional macroinitiators were used in the synthesis of di- and triblock copolymers of polydiethylsiloxane and polystyrene by the controlled radical polymerization (Scheme 4).



Scheme 4. Syntheses of the di- and triblock copolymers of AB and ABA types, where A is polystyrene and B is polydiethylsiloxane.

Figures 5a and 5b show the GPC curves of the AB and ABA copolymers, respectively.

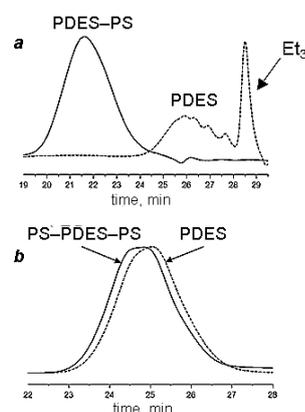


Figure 5. GPC curves: (a) initial monofunctional macroinitiator α -butyl- ω -[(4-chloromethylphenylethyl)dimethylsiloxy]oligodiethylsiloxane (PDES) and the resulting PDES-PS diblock copolymer (chloroform); (b) initial bifunctional macroinitiator α,ω -bis-[(4-chloromethylphenylethyl)dimethylsiloxy]polydiethylsiloxane (bifunctional PDES) and the resulting PS-PDES-PS triblock copolymer (THF).

The chemical structures of the resulting copolymers were studied by NMR spectroscopy (Fig. 6). According to the results obtained, the ratio of the PS/PDES blocks in the diblock copolymer composed 10.6/1 (Fig. 6a). The integration of the signals of styrene protons in the spectrum of the triblock copolymer was complicated due to low signal intensities.

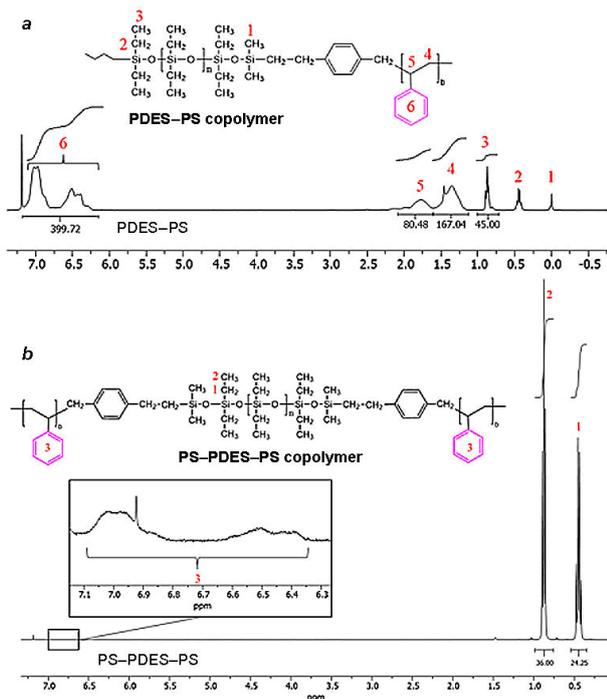


Figure 6. ^1H NMR spectra: (a) PDES–PS diblock copolymer derived from the copolymerization of monofunctional initiator α -butyl- ω -[(4-chloromethylphenylethyl)dimethylsiloxy]oligodiethylsiloxane with styrene; (b) PS–PDES–PS triblock copolymer derived from the copolymerization of bifunctional initiator α,ω -bis-[(4-chloromethylphenylethyl)dimethylsiloxy]polydiethylsiloxane (bifunctional PDES) with styrene.

The low activity of benzyl chloride moieties hampers free variation of the block ratios; therefore, further investigations with these promising objects will be switched to the macroinitiators bearing benzyl bromide residues. It is important to note that a general scheme for the synthesis of block copolymers using PDES macroinitiators will be fully reproduced.

Experimental

General remarks

N,N,N',N''-Pentamethyldiethylenetriamine (PMDETA, >97%, Sigma Aldrich), *o*-xylene (anhydrous, 97%, Sigma Aldrich), copper chloride (>99.999%, Sigma Aldrich), platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (Sigma Aldrich), *n*-BuLi solution (1.6 M in hexanes, Acros Organics), 4-vinylbenzyl chloride (95%, Acros Organics), and chlorodimethylsilane (99.5%, abcr) were purchased from commercial sources and used without purification. Styrene (St) (98%, Sigma Aldrich) was passed through a basic alumina column to remove an inhibitor. KOH (chem. pure, 85%) and organic solvents, such as tetrahydrofuran, chloroform, toluene, dimethylformamide, and methanol purified by standard procedures [22, 23] were also used in the experiments. Hexaethylcyclotrisiloxane was obtained according to the previously published method [24] and distilled over CaH_2 .

Gas–liquid chromatography was carried out on a Khromatek Analitik 5000 chromatograph (Russia) using a katharometer detector, helium as a carrier gas, columns 2 m \times 3

mm, SE-30 (5%) applied to Chromaton-H-AW as an immobile phase, and Khromatek Analitik software (Russia).

Gel permeation chromatography (GPC) was carried out on a unit consisting of a Bischoff HPLC pump, a Jasco 2035-plus refractive index detector, and four MZ-DVB columns with the pore sizes of 30 Å, 100 Å, and 2×3000 Å. THF or chloroform bearing 1.0 g/L of LiBr was used as an eluent at the flow rate of 1.0 mL/min. The molecular masses were defined based on a calibration curve for a polydimethylsiloxane standard.

^1H NMR spectra were registered on a Bruker WP-250 SY spectrometer at the frequency of 250 MHz using tetramethylsilane as an external standard and CDCl_3 as a solvent. The spectra were processed using ACD/Labs software.

Syntheses

Synthesis of α -butyl- ω -(lithiumoxy)oligodiethylsiloxane.

The polymerization was carried out in an inert atmosphere. The reaction flask equipped with a magnetic stirring bar and a reflux condenser was charged with hexaethylcyclotrisiloxane (2.80 g, 9.20 mmol), *n*-BuLi solution (1.15 mL, 1.83 mmol), and toluene (3.20 mL). The stirring (initiation) was carried out at room temperature for 20 h. Then, DMF (0.43 mL, 1.83 mmol) was added, and the resulting mixture was heated at 60 °C for 6 h.

Synthesis of α,ω -dipotassioxyoligodiethylsiloxane. The polymerization was carried out in an inert atmosphere. The reaction flask equipped with a magnetic stirring bar and a reflux condenser was charged with hexaethylcyclotrisiloxane (2.355 g, 7.700 mmol) and KOH (0.009 g, 0.162 mmol). The polymerization was carried out at 150 °C for 1 h and afforded a highly viscous turbid product.

Synthesis of chloro(dimethyl)-(4-chloromethylphenylethyl)silane. The platinum catalyst (PCO72, 94 μL) was added to a solution of 4-vinylbenzyl chloride (30.00 g, 0.24 mol) and chlorodimethylsilane (33.30 g, 0.36 mol) in toluene (31 mL). The temperature of the reaction mixture increased to 55 °C. Then, it was stirred at room temperature for 7 h. The solvent was removed under reduced pressure. The vacuum distillation of the resulting residue afforded a fraction (a mixture of isomers) with the content of the main compound of 96%. Yield: 85%.

^1H NMR: δ 0.29–0.37 ($(\text{CH}_3)_2\text{SiCl}$), 0.38–0.49 ($(\text{CH}_3)_2\text{SiCl}$), 1.12–1.24 ($-\text{CH}_2-\text{CH}_2(\text{Ph})-$), 1.42–1.51 ($-\text{CH}_3-\text{CH}(\text{Ph})-$), 2.39–2.50 ($-\text{CH}_3-\text{CH}(\text{Ph})-$), 2.72–2.81 ($-\text{CH}_2-\text{CH}_2(\text{Ph})-$), 4.58 ($-\text{CH}_2\text{Cl}$), 7.08–7.37 ($-\text{C}_6\text{H}_4-$) ppm.

Synthesis of α -butyl- ω -[(4-chloromethylphenylethyl)dimethylsiloxy]oligodiethylsiloxane. Chloro(dimethyl)-(4-chloromethylphenylethyl)silane (0.47 g, 1.83 mmol) was added to a mixture of α -butyl- ω -(lithiumoxy)oligodiethylsiloxane in an inert atmosphere at +5 °C. The reaction time was 3 h. LiCl was filtered off and rinsed with the same solvent (toluene). The resulting filtrate was evaporated under reduced pressure to give the target product.

^1H NMR: δ 0.06–0.13 ($(\text{CH}_3)_2\text{ClSi}-$), 0.42–0.65 ($\text{CH}_3-\text{CH}_2-\text{Si}-$), 0.83–1.02 ($\text{CH}_3-\text{CH}_2-\text{Si}-$), 1.25–1.38 ($-\text{CH}_2-\text{CH}_2(\text{Ph})-$), 2.59–2.68 ($-\text{CH}_2-\text{CH}_2(\text{Ph})-$), 4.57 ($-\text{CH}_2\text{Cl}$), 7.14–7.33 ($-\text{C}_6\text{H}_4-$) ppm.

Synthesis of α,ω -bis-[(4-chloromethylphenylethyl)dimethylsiloxy]polydiethylsiloxane. Chloro(dimethyl)-(4-chloromethylphenylethyl)silane (0.94 g, 1.83 mmol) was added

to a mixture of α -butyl- ω -(lithiumoxy)oligodiethylsiloxane in toluene in an inert atmosphere at +5 °C. The reaction time was 3 h. LiCl was filtered off and rinsed with the same solvent (toluene). The resulting filtrate was evaporated under reduced pressure to give the target product.

^1H NMR: δ 0.35–0.51 ($\text{CH}_3\text{-CH}_2\text{-Si-}$), 0.81–0.96 ($\text{CH}_3\text{-CH}_2\text{-Si-}$), 7.08–7.23 ($-\text{C}_6\text{H}_4\text{-}$) ppm.

Synthesis of the PDES–PS diblock copolymer by the copolymerization of α -butyl- ω -[(4-chloromethylphenylethyl)dimethylsiloxy]oligodiethylsiloxane with styrene. α -Butyl- ω -[(4-chloromethylphenylethyl)dimethylsiloxy]oligodiethylsiloxane ($M_n = 1350$; 0.50 g, 0.31 mmol), St (3.25 g, 31 mmol), PMDETA (0.26 mL, 1.24 mmol), CuCl (62 mg, 0.62 mmol) (ratio of the reagents: 1:100:4:2), and *o*-xylene (3.6 mL) were placed into a flask, which was then connected to a Schlenk line and degassed using freeze-pump-thaw cycling (three times). Then, the reaction flask with the reagents was immersed into an oil bath heated to 130 °C. The mixture was stirred for 3 h. The reaction was terminated by filling the flask with air and placing it into liquid nitrogen. Then, the resulting mixture was dissolved in toluene and passed through a basic alumina column. The block copolymer was isolated by triple precipitation using centrifugation in a methanol/toluene system. The low-molecular compounds were removed at 80 °C and the residual pressure of 0.03 mbar to give the target diblock copolymer as a transparent colorless glassy product. Yield: 1 g (27%).

^1H NMR: δ 0.1 ($\text{CH}_3\text{Si-}$), 0.33–0.52 ($-\text{Si-CH}_2\text{-}$), 0.72–0.95 ($-\text{Si-CH}_2\text{-CH}_3$), 1.18–1.58 ($-\text{CH}_2\text{-CH(Ph)-}$), 1.58–1.95 ($-\text{CH}_2\text{-CH(Ph)-}$), 6.17–6.68 ($-\text{C}_6\text{H}_4\text{-}$), 6.78–7.12 ($-\text{C}_6\text{H}_4\text{-}$) ppm.

Synthesis of the PS–PDES–PS triblock copolymer by the copolymerization of α,ω -bis-[(4-chloromethylphenylethyl)dimethylsiloxy]polydiethylsiloxane with styrene. The reaction was carried out analogously to the synthesis of the PDES–PS diblock copolymer using α,ω -bis-(4-chloromethylbenzyl)polydiethylsiloxane ($M_n = 85500$; 0.50 g, 0.006 mmol), St (0.24 g, 2.300 mmol), PMDETA (4.9 μL , 0.023 mmol), and CuCl (1.16 mg, 0.012 mmol) (ratio of the reagents: 1:400:4:2) at 130 °C for 3 h. The target triblock copolymer was isolated as a transparent glassy product. Yield: 0.42 g (70%).

^1H NMR: δ 0.1 (CH_3Si), 0.33–0.52 ($\text{Si-CH}_2\text{-}$), 0.72–0.95 ($\text{Si-CH}_2\text{-CH}_3$), 1.18–1.58 ($-\text{CH}_2\text{-CH(Ph)-}$), 1.58–1.95 ($-\text{CH}_2\text{-CH(Ph)-}$), 6.17–6.68 ($-\text{C}_6\text{H}_4\text{-}$), 6.78–7.12 ($-\text{C}_6\text{H}_4\text{-}$) ppm.

Conclusions

To summarize the results presented, we succeeded in the synthesis of the mono- and bifunctional polydiethylsiloxane macroinitiators featuring terminal 4-chloromethylphenylethyl residues and the following molecular mass characteristics: $M_n = 1350$ and $M_w/M_n = 1.15$ (in the case of the monofunctional derivative), $M_n = 85500$ and $M_w/M_n = 1.31$ (in the case of the bifunctional counterpart). The resulting macroinitiators were used to obtain the di- and triblock copolymers of polydiethylsiloxane and polystyrene. Despite the successful realization of a general scheme for the synthesis of triblock copolymers, we failed to obtain the ABA copolymers with the variable length of the polystyrene block due to the low activity of benzyl chloride residues in the PDES macroinitiator. Nevertheless, since the general concept of the use of PDES macroinitiators fully justified itself, we will reproduce it with

benzyl bromide substituents and, thus, synthesize a representative series of new PS–PDES–PS block copolymers featuring various molecular parameters.

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