



## SYNTHESIS OF POLYDIETHYLSILOXANE MACROMONOMERS

Cite this: *INEOS OPEN*,  
2024, 7 (1–3), 57–58  
DOI: 10.32931/io2424a

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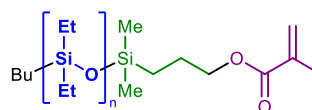
Received 10 May 2024,  
Accepted 27 May 2024

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### Abstract

This paper describes the synthesis of polydiethylsiloxane (PDES) macromonomers of  $\alpha$ -butyl- $\omega$ -dimethylsilylpropyl methacrylate oligodiethylsiloxanes with  $M_n$  from 1400 to 6400. The macromonomers were obtained by the anionic polymerization of hexaethylcyclotrisiloxane followed by the treatment of the lithium oxy group with 3-(chlorodimethylsilyl)propyl methacrylate. The resulting macromonomers were characterized by <sup>1</sup>H NMR spectroscopy and gel permeation chromatography (GPC).



**Key words:** anionic polymerization, polydiethylsiloxane, polymer brushes.

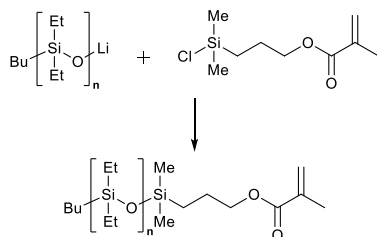
### Introduction

Over recent years, considerable attention has been paid to the investigation of cylindrical polymer brushes (CPBs) [1]. Their synthesis is performed using grafting to, grafting from, and grafting through strategies [2, 3].

This communication presents the method of obtaining polydiethylsiloxane macromonomers for their further application in the synthesis of CPBs using the grafting through method.

### Results and discussion

The synthesis of PDES macromonomers was carried out in two stages. At the first stage, the anionic polymerization of hexaethylcyclotrisiloxane was carried out in the presence of *n*-BuLi according to the published procedure [4]. At the second stage, resulting  $\alpha$ -butyl- $\omega$ -(lithiumoxy)polydiethylsiloxane was treated with 3-(chlorodimethylsilyl)propyl methacrylate, affording a series of PDES macromonomers featuring terminal methacrylate groups and  $M_n$  from 1400 to 6400 (Scheme 1).



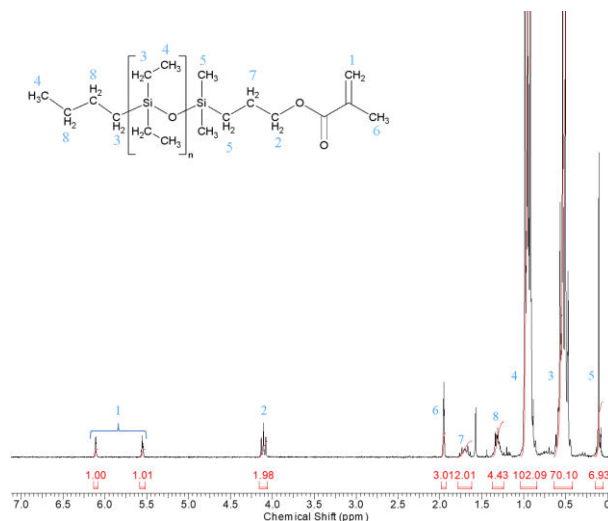
**Scheme 1.** Synthesis of the PDES macromonomers.

The molecular weight characteristics of the resulting macromonomers are presented in Table 1.

**Table 1.** Molecular weight characteristics of the resulting PDES macromonomers

No.	PDES polymerization degree theoretical/GPC/NMR	$M_n$	$M_w$	$M_w/M_n$
1	15/13/13	1400	2100	1.51
2	15/19/17	1900	2900	1.52
3	68/61/58	6400	7500	1.17
4	15/15/15	1400	2300	1.57

The chemical structures of all the macromonomers obtained were confirmed using <sup>1</sup>H NMR spectroscopy. Since the <sup>1</sup>H NMR spectra of the macromonomers differed only in the number of units in the main chain, Fig. 1 depicts the <sup>1</sup>H NMR spectrum of one of the macromonomers used as an example (Table 1, no. 3).



**Figure 1.** <sup>1</sup>H NMR spectrum of the selected PDES macromonomer.

The resulting macromonomers were used to obtain polymer brushes by the atom transfer radical polymerization (ATRP) method. The conversion of the macromonomers varied from 60 to 77% depending on the reaction time from 11.5 to 200 h, respectively. A more detailed study of the new type of polymer architectures is the subject of our further research.

## Experimental section

### General remarks

Tris[2-(dimethylamino)ethyl]amine (98%, ABCR), ethyl 2-bromoisobutyrate (98%, Alfa Aesar), *p*-xylene (97%, Sigma), copper(I) chloride (>99.999%, Sigma Aldrich), *n*-butyllithium (1.6 M, Acros Organics), allyl methacrylate (98%, Acros Organics), dimethylchlorosilane (DMCS) (99.5%, ABCR), and Karstedt's catalyst (2.1–2.4% Pt, ABCR) were purchased from commercial sources and used without further purification. The following solvents were used in the syntheses: toluene, ethyl acetate, tetrahydrofuran (THF), benzene, and dimethylformamide (DMF). They were processed according to the standard methods [5]. Hexaethylcyclotrisiloxane was obtained by the published procedure [6].  $\alpha$ -Butyl- $\omega$ -(lithiumoxy)polydiethylsiloxane [4],  $\alpha$ -butyl- $\omega$ -(dimethylsilyl)propyl methacrylate polydiethylsiloxanes with different molar masses and 3-(chlorodimethylsilyl)propyl methacrylate were synthesized according to the procedures described in Refs. [7] and [8], respectively.

The  $^1\text{H}$  NMR spectra were recorded on a Bruker WP 250 SY spectrometer (Germany). The solvent was  $\text{CDCl}_3$ . The spectra were processed using the ACD LABS software package. The GPC analysis was performed on the following chromatographic system: LC-10ADvp high-pressure pump (Shimadzu, Japan), Smartline RI 2300 refractive index detector, and JETSTREAM 2 PLUS thermostat (KNAUER, Germany). The temperature was  $40 \pm 0.1$  °C, the eluent was toluene + 2% of THF, the flow rate was 1.0 mL/min. The columns in use were Phenogel 5  $\mu\text{m}$  columns ( $300 \times 7.8$  mm, Phenomenex, USA) with the pore sizes from 50 to  $10^5$  Å. The columns were calibrated relative to the Agilent polystyrene standards (USA). The processing of the chromatograms and calculation of the molecular weight characteristics were performed using MultiChrom software for Windows version 1.6. (Ampersend, Russia).

### Syntheses

#### General procedure for the synthesis of polydiethylsiloxane macromonomers.

3-(Chlorodimethylsilyl)propyl methacrylate (0.0937 g, 0.404 mmol) and dry toluene (2 mL) were placed in a round-bottomed flask equipped with a magnetic stirrer, thermometer, and dropping funnel. After cooling the reaction mixture to  $-50$  °C, a solution of PDES containing a lithium oxy group (4.0960 g, 0.630 mmol) in dry toluene (8 mL) was added dropwise upon vigorous stirring. All manipulations were carried out under an

atmosphere of dry argon. The reaction mixture was stirred for several hours. After the reaction completion, the product was filtered from the precipitate. The excess solvent was removed on a membrane evaporator, and its residues were removed on an oil pump.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.1 ( $\text{SiCH}_3$ ), 0.4 ( $\text{SiCH}_2\text{CH}_3$ ), 0.8 ( $\text{SiCH}_2\text{CH}_3$ ), 1.9 ( $\text{CH}_3\text{C}=\text{CH}_2$ ), 4.1 ( $\text{CH}_2\text{CH}_2\text{O}$ ), 5.5 ( $\text{C}=\text{CH}_2$ ), 6.3 ( $\text{C}=\text{CH}_2$ ) ppm.

## Conclusions

Polydiethylsiloxane macromonomers featuring terminal methacrylate groups and  $M_n$  from 1400 to 6400 were obtained by the anionic polymerization followed by the treatment of the lithium oxy group with 3-(chlorodimethylsilyl)propyl methacrylate. The resulting compounds were characterized by GPC and  $^1\text{H}$  NMR spectroscopy. The macromonomers obtained were used to produce polymer brushes by the grafting through method, the study of the properties of which will be the subject of the following reports.

## Acknowledgements

This work was supported by the Russian Science Foundation (project no. 21-73-30030).

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