



# PREPARATION OF POLYDIMETHYLSILOXANE COPOLYMERS BY THE AZIDE–ALKYNE HUISGEN CYCLOADDITION METHOD

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## Abstract

The copolymers containing alternating siloxane and urethane units in the chain as well as ester moieties were synthesized by the azide–alkyne cycloaddition without application of a solvent and copper salts as catalysts. The resulting copolymers were analyzed by NMR spectroscopy and gel permeation chromatography.

**Key words:** polydimethylsiloxanes, urethanes, copolymers, click chemistry, cycloaddition.

## Introduction

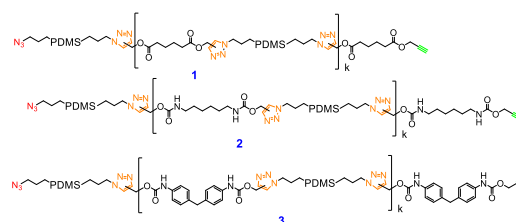
Polydimethylsiloxanes (PDMSs) are extensively used in research and industry owing to their unique properties, such as chemical inertness, high elasticity, biocompatibility, wide range of operating temperatures, hydrophobicity, resistance to ultraviolet radiation and others. However, their main drawback is the low mechanical strength, which limits their application scope [1–3].

The azide–alkyne cycloaddition reaction catalyzed by monovalent copper salts (CuAAC) is a versatile and simple approach that ensures efficient interaction between molecules, including polymeric systems, under different conditions and allows achieving a stereoregular structure of the product under mild conditions [4, 5]. It allows for a modular assembly of polymers and easy alternation of the units. However, the presence of catalyst impurities in the resulting compound may be undesirable (*e. g.*, for *in vivo* application).

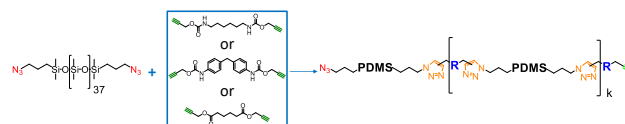
The use of the 1,3-dipolar azide–alkyne Huisgen cycloaddition implies the reaction proceeding without the participation of copper salts and allows obtaining a product that does not require the purification from the catalyst. However, this approach has disadvantages such as non-stereoselectivity of the resulting compounds (a mixture of 1,4- and 1,5-triazoles) and more severe reaction conditions (the temperature above 100 °C). This method is often used to modify polymers and to cross-link silicones [6]. Therefore, the goal of this study was to obtain PDMS copolymers with urethane/ester units in the main polymer chain by the AAC method without copper catalysts.

## Results and discussion

A series of copper-free azide–alkyne cycloaddition reactions



were carried out using blocked alkyne difunctional monomers and telechelic PDMS (Scheme 1). The reactions were carried out upon stirring in an oil bath at 140 °C. The reaction course was monitored using <sup>1</sup>H NMR spectroscopy by the disappearance of -CH<sub>2</sub>-N<sub>3</sub> signals of the propylene unit at 3.24 ppm.



**Scheme 1.** General scheme of the azide–alkyne cycloaddition.

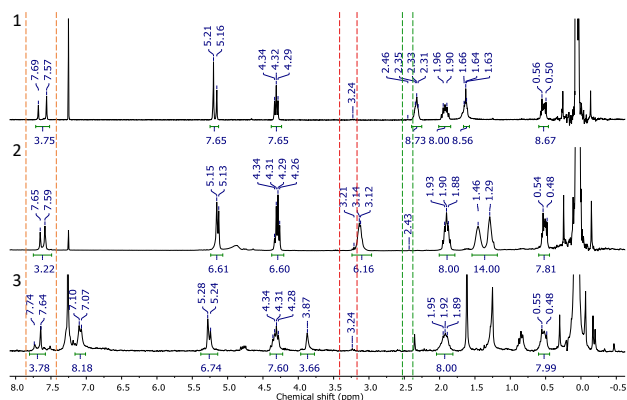
The resulting copolymers were analyzed by <sup>1</sup>H NMR spectroscopy (Fig. 1). The spectra revealed the absence of signals at 2.43–2.46 and 3.24, which correspond to the signals of the acetylene and CH<sub>2</sub> units at the azide group, and the appearance of signals at 7.57–7.74, which correspond to the signals of a mixture of 1,4- and 1,5-triazoles.

The ratio of the integral intensities of the proton signals corresponded to the expected one.

The copolymers were also studied by gel permeation chromatography (GPC). The results obtained are presented in Table 1. The number-average molecular weight varied from ~10000 to 14000 amu. The polydispersity index ranged from 1.9 to 2.8.

**Table 1.** Results of the GPC analysis of the copolymers obtained

Copolymer	$M_n$	$M_w$	$M_w/M_n$
1	10900	20900	1.94
2	14300	30900	2.16
3	12200	34900	2.85



**Figure 1.** Comparison of the  $^1\text{H}$  NMR spectra of the resulting copolymers.

## Experimental section

### General remarks

Propargyl alcohol (99%), adipic acid (ABCR), benzene (reagent grade, Khimmed), and *p*-toluenesulfonic acid (Ruskhim) were purchased from commercial sources. Bis(3-azidopropyl)polydimethylsiloxane with a molecular weight of 3000 amu [7], di(prop-2-yn-1-yl) hexane-1,6-diyl dicarbamate [8], and di(prop-2-yn-1-yl) [methylenebis(4,1-phenylene)]dicarbamate [9] were synthesized according to the published procedures.

### Analysis and general methodology

The GPC analysis was performed on a Shimadzu LC-10A series chromatograph (Japan) equipped with an RID-10A refractometer and SPD-M10A diode matrix detectors. The analytical separation was performed using a 7.8 mm  $\times$  300 mm Phenomenex column (USA) filled with Phenogel sorbent with pore sizes of 15–500 Å. THF was used as an eluent. Polystyrene was used as a standard. The temperature was  $40 \pm 0.1$  °C. The flow rate was 1 mL/s.

The  $^1\text{H}$  NMR spectra were recorded at room temperature on a Bruker Avance 300 spectrometer (Mannheim, Germany) in  $\text{CDCl}_3$ . The spectra were processed using the MestReNova software (v. 12.0). The residual solvent signal (7.26 ppm) was used to reference the  $^1\text{H}$  NMR spectra.

### Syntheses

The detailed procedures for the synthesis of the copolymers are presented in the ESI.

## Conclusions

The copper-free AAC reactions afforded the triazole-containing copolymers with alternating fragments based on oligomeric polydimethylsiloxane and urethanes or esters in the main polymer chain. The resulting copolymers were studied by GPC and NMR spectroscopy. The occurrence of the click reaction and the formation of polydimethylsiloxane–triazole copolymers with the average molecular weights ranging from 10000 to 14000 amu were confirmed.

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## Electronic supplementary information

Electronic supplementary (ESI) information available online: the  $^1\text{H}$  NMR spectra, GPC curves, and synthetic procedures for di(prop-2-yn-1-yl) adipate. For ESI, see DOI: 10.32931/io2404a.

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