



Article Click Addition Reaction of Urethane–Acrylate Resin Using Octa(3-thiopropyl)silsesquioxane Derivatives as Cross-Linking Agents

Daria Pakuła ^{1,2}, Bogna Sztorch ², Robert E. Przekop ^{2,*} and Bogdan Marciniec ^{1,2,*}

- ¹ Faculty of Chemistry, Adam Mickiewicz University in Poznań, ul. Uniwersytetu Poznańskiego 8, 61-614 Poznan, Poland; darpak@amu.edu.pl
- ² Centre for Advanced Technologies, Adam Mickiewicz University in Poznan, ul. Uniwersytetu Poznańskiego 10, 61-614 Poznan, Poland; bogna.sztorch@amu.edu.pl
- * Correspondence: robert.przekop@amu.edu.pl (R.E.P.); bogdan.marciniec@amu.edu.pl (B.M.)

Abstract: In this work, new partially substituted derivatives of octa(3-thiopropyl)silsesquioxane (SSQ-8SH) were synthesized. The article compares the thiol-ene reaction using two methods: radical mechanism, thermally initiated (AIBN), and in the presence of a photoinitiator (DMPA). Both the crystalline and the oil forms of SSQ-8SH were functionalized. Olefins with nonpolar alkyl groups (hexene, octene, and octadecene) and vinyltrimethoxysilane, allyl glycidyl ether, allyl 2,2,3,3,4,4,5,5-octafluoropentylether, allyl methacrylate, and styrene were used in the reactions, allowing to obtain seven new derivatives. All compounds were characterized using spectroscopic (¹H NMR and ²⁹Si NMR) and spectrometric (MALDI-TOF-MS) methods. The influence of functional groups on the water contact angle value was determined. The functionalization of the compound led to a contact angle value above 95° (SSQ-4SH-4OD). Density measurements and thermogravimetric analysis (TGA) were carried out for all compounds. The highest onset temperature (357.4 °C) and temperature at the maximum mass loss rate (377.3 °C) were observed for SSQ-SH-4OD. The addition of alkyl groups significantly decreased the density of compounds with increasing chain length (1.198 g/cm³; 1.162 g/cm³; 1.095 g/cm³ for hexene, octene, and octadecene, respectively). Silsesquioxanes have potential applications in various materials, such as UV-curable resins, allowing to modify, for example, their surface properties. Modification of a commercial photocurable resin with selected derivatives was carried out to determine the impact on physicochemical properties (TGA, WCA).

Keywords: thiol-ene; silsesquioxane; resin; urethane-acrylate resin; photopolymerization; 8SH-POSS

1. Introduction

The reaction between a thiol group and a reactive carbon–carbon double bond has been extensively studied in the literature for over a century. The reaction, known as a thiol-ene, was first described by Theodor Posner in 1905, when he detailed the reactions between mercaptans and aliphatic olefins, aromatic olefins, aliphatic diolefins, aromatic diolefins, cyclic diolefins, and terpenes [1]. However, it was only after 2002 that there was a surge in interest in thiol-ene reactions, resulting in scientific publications (based on Scopus analysis, Figure 1). In the years 1972–2002, the number of articles available in the Scopus database according to the search keyword "thiol-ene" is 51. From 2003 to 2022, 4373 scientific articles were published, which shows the scale of interest in the reaction belonging to click-chemistry. The largest number of scientific articles was published in 2020 (432 publications). The analysis also revealed a niche in the use and modification of octa(3-thiopropyl)silsesquioxane.

Hydrothiolation is a widely used process due to its fast reaction rate, relatively mild conditions, high conversion, minimal or no by-products, variety of substrates, and high selectivity [2,3]. It has numerous applications, including in protective coatings,



Citation: Pakuła, D.; Sztorch, B.; Przekop, R.E.; Marciniec, B. *Click* Addition Reaction of Urethane–Acrylate Resin Using Octa(3-thiopropyl)silsesquioxane Derivatives as Cross-Linking Agents. *Processes* **2023**, *11*, 3285. https://doi.org/10.3390/ pr11123285

Academic Editor: Mohammad Boshir Ahmed

Received: 7 November 2023 Revised: 20 November 2023 Accepted: 21 November 2023 Published: 24 November 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). peptides [4], preparation of dendrimers [5], modification of materials [6,7], optical materials [8], ionogels [9], or hydrogels [10]. The thiol-ene reaction can be carried out by either radical or ionic means. In 2010, Charles Hoyle and Christopher Bowman published reviews [2] which described the mechanisms of the thiol-ene reaction. Reactions carried out in an electrophilic manner with the use of an acid lead obtain branched products according to Markovnikov's rule [11,12]. The ionic reaction using a base as the initiator, on the other hand, leads to products that do not follow Markovnikov's rule (linear products) and is also called the Michael addition reaction. The use of primary amine [13] and phosphines [14,15] as nucleophilic addition initiators is known in the literature. The ionic mechanism can also proceed without the use of a catalyst, but for the reaction to occur, the substrates must be characterized by high reactivity [16]. Radical synthesis leads to obtaining linear products inconsistent with Markovnikov's rule. They can take place in the presence of a photoinitiator or a thermal initiator, but also, for highly reactive substrates, without an initiator [17]. The radical reaction between the thiol and unsaturated bonds proceeds similarly to the mechanism of chain transfer polymerization. The first step involves the generation of the thivl radical (initiation). The obtained thivl radical takes part in the second step (propagation), which consists of the direct addition of the radical to the C=C bond, giving an intermediate radical on the carbon centre, and then transferring the chain to the second thiol molecule, which gives the anti-Marcovnikov addition product. At the same time, a new thiyl radical is generated, which can be used in the propagation or termination step [18,19]. In a radical way, side reactions can also occur, such as homopropagation, homopolymerization initiation, and disulfide formation. Simple reaction mechanisms of thiol-ene in the presence of AIBN or DMPA are shown in Figure 2.



Figure 1. Scopus analysis of the thiol-ene reaction.



Figure 2. General reaction scheme of thiol-ene (**A**) with a DMPA initiator [20]; (**B**) with an AIBN initiator [21].

Octa(3-thiopropyl)silsesquioxane (both crystalline and oil products of 3-thiopropyltrimethoxysilane condensation) were functionalized through the thiol-ene reaction. Silsesquioxanes (SSQ) belong to hybrid inorganic-organic compounds with the general formula (RSiO_{1.5})_n, where R is an organic group or hydrogen [22]. They consist of a stable inorganic Si-O core and reactive or inert organic groups linked directly to the silicon atom or via a dimethylsiloxy moiety. The attached functional group determines their physicochemical properties, e.g., melting point, hydrophilic-hydrophobic, and adhesive properties, as well as their catalytic capabilities. Silsesquioxanes can have a random, ladder, or cage structure (fully or partially closed), where the most popular is the T_8 structure [23,24]. These compounds are used as additives in (nano)composites [25–30], as precursors of porous materials [31,32], in electronics [33], in catalysis [34,35], and as a flame retardant [36]. The preparation of octa-substituted silsesquioxane with thiopropyl groups and its physicochemical characteristics are described in the literature [37]; however, there are only few literature reports of its modifications. Examples of the thiol-ene reaction between SSQ-8SH and allyl alcohol, 2-allyloxyethanol, 6-chloro-1-hexene, 6-bromo-1-hexene, styrene, and eugenyl methacrylate are known [38]. Other examples indicate a reaction between SSQ-8SH and 1,4-divinylbenzene, methacrylate ethyl trimethyl ammonium chloride [39], 2-(perfluorooctyl) ethyl acrylate [40], 9-vinyl carbazole [41], 1-methyl-3-butenylimidazolium bromide, 1-methyl-3-pentenylimidazolium bromide, 1-pentafluorobenzene-4-allylpyridinium bromide, 1-butyl-4-allylpyridinium bromide [42], 2-methacryloyloxyethylphosphorylcholine, or allylphosphorylcholine [43]. Our previous work presents the functionalization of octa(3-thiopropyl)silsesquioxane (SSQ-8SH) via radical reaction in the presence of azobisisobutyronitrile (AIBN) [44]. In Professor Maciejewski's group, silsesquioxanes with sulfur atoms in the structure were obtained through hydrothiolation of (ViSiMe₂O)₈Si₈O₁₂. The obtained products were used for the hydrophobization of fabrics [45].

This work presents the preparation of partially substituted octa(3-thiopropyl)silsesquioxane derivatives and discusses the differences in the synthesis via the radical route using a thermally activated initiator (azobisisobutrylonitriles-AIBN) and via photoaddition in the presence of 2,2-dimethoxy-2-phenylacetophenone (DMPA). Figure 2 shows the general mechanisms of the thiol-ene reaction activated by AIBN and DMPA. The tests were carried out on a crystalline and oil product, which allowed to determine the influence of the SSQ-8SH form on the course of the reaction. The functionalization was performed with the following olefins: hexene (HEX), octene (OCT), octadecene (OD), vinyltrimethoxysilane (VTMOS), allyl glycidyl ether (AGE), allyl 2,2,3,3,4,4,5,5-octafluoropentylether (Allyl-OFP), allyl methacrylate (MA), and styrene (STYR). The obtained products were characterized spectroscopically (¹H NMR and ²⁹Si NMR) and spectrometrically (MALDI-TOF-MS). Density measurements and thermogravimetric analysis (TGA) were performed to determine the physicochemical properties. Tests with a goniometer apparatus were carried out to determine the influence of functional groups on the water contact angle value. Modification of a commercial photocurable resin with selected derivatives was carried out to determine the impact on physicochemical properties (TGA, WCA).

2. Materials and Methods

2.1. Chemicals

The chemicals were purchased from the following sources: 3-mercaptopropyltrimethoxysilane (99%) and vinyl(trimetoxy)silane (VTMOS) (97%) from UNISIL (Tarnów, Poland); methanol p.a. from P.P.H Stanlab (Lublin, Poland); hydrochloric acid (35–38%), toluene, tetrahydrofuran, and dichloromethane from Chempur (Piekary Śląskie, Poland); azoisobutyronitrile (AIBN) (98%), hexene (HEX) (97%) and allyl methacrylate (MA) (98%), allyl glycidyl ether (AGE) (98%) from Thermo Scientific Chemicals (Waltham, MA, USA); octene (OCT) (97%) from ABCR (Karlsruhe, Germany), octadecene (OD) (97%), styrene (STYR), and dimethoxy- α -phenylacetophenone (DMPA), chloroform-d from Merck Group (Darmstadt, Germany). Allyl 2,2,3,3,4,4,5,5-octafluoropentyl ether (Allyl-OFP) was synthesized according to the literature [46]. Toluene was degassed and dried by distilling it from P₂O₅ under an argon

atmosphere. Difunctional aliphatic urethane-acrylate resin (Ebecryl 1271) was purchased from Allnex (Frankfurt, Germany).

2.2. Analytical Methods and Methodology

The ¹H NMR spectra were recorded on a Bruker Ultrashield 300 MHz. The ²⁹Si NMR spectra were recorded on a Bruker Ascend 400 MHz operating at 101 and 79 MHz, respectively. Chloroform-*d* was used as a solvent.

MALDI-TOF mass spectra were recorded on a UltrafleXtreme mass spectrometer (Bruker Daltonics) equipped with a SmartBeam II laser (355 nm) in the 500–4000 m/z range, and 2,5-dihydroxybenzoic acid (DHB, Bruker Daltonics, Bremen, Germany) served as the matrix.

Contact angle analysis (WCA) was performed using the sessile drop technique at room temperature and atmospheric pressure, with a Krüss DSA100 goniometer (Krüss, Hamburg, Germany). Three independent measurements were performed for each sample, each with a 5 μ L water drop, and the obtained results were averaged to reduce the impact of surface nonuniformity.

Density measurement was performed on a Laboratory Density Meter DDM 2911 by Rudolph Research Analytical (Hackettstown, NJ, USA). The apparatus made 3 measurements at 25 $^{\circ}$ C for each sample, which were then averaged.

Thermogravimetry (TGA) was performed using a NETZSCH 209 F1 Libra thermogravimetric analyzer (NETZSCH, Selb, Germany). Samples of 4 ± 0.2 mg were placed in Al₂O₃ crucibles. Measurements were conducted under nitrogen (flow of 20 mL/min) in the range of 30–950 °C and with a 10 °C/min heating rate.

Images of samples were taken with the digital light microscope Keyence VHX-7000 (Keyence International NV/SA, Osaka, Japan) with a VH-Z100R wide-angle zoom lens (Keyence International NV/SA, Osaka, Japan) at 100× magnification.

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet iS50 Fourier transform spectrophotometer (Thermo Fisher Scientific, Warsaw, Poland).

2.3. Synthesis of Precursor Octa(3-thiopropyl)silsesquioxane

Octa(3-thiopropyl)silsesquioxane was prepared according to the literature [37,47] and our previous article [44].

2.4. General Procedure for Thiol-Ene Tests with Octa(3-thiopropyl)silsesquioxane in the Presence of AIBN

The thiol-ene reactions were carried out under an inert gas atmosphere in Schlenk vessels equipped with a magnetic stirrer. A total of 0.04921 mmol (50 mg) of crystalline SSQ-8SH, 1 equivalent of olefin per -SH group (4 groups), 3 mL of toluene, and 0.1 equivalents of AIBN relative to the -SH group were placed in the reactor. The mixture was heated to 65 °C and vigorously stirred for 24 h. Then, the solvent was evaporated under a vacuum to dryness. The progress of the reaction was controlled by ¹H NMR. The NMR spectroscopy confirmed the structures of the products, where the assigned signals were as follows: SSQ-4SH-4HEX

 $\begin{array}{c} C_{\theta}H_{13} \\ HS \\ HS \\ C_{\theta}H_{13}-S \\ HS \\ C_{\theta}H_{13}-S \\ C_{\theta}H_{13$

Chemical Formula: C48H104O12S8Si8

¹H NMR (400 MHz, CDCl₃): δ(ppm) = 2.72–2.62 (m, 4H, alpha product S<u>CH</u>(CH₃)CH₂(CH₂)₂CH₃), 2.56–2.48 (m, 24H, -<u>CH₂SCH₂-</u>), 1.73–1.65 (m, 16H, SiCH₂<u>CH₂</u>CH₂S), 1.59–1.53 (m, 8H, SCH₂<u>CH₂(CH₂)₃CH₃, alpha product SCH(CH₃)CH₂(CH₂)₂CH₃), 1.40–1.35 (m, 4H, SH),</u>

1.33–1.24 (m, 24H, SCH₂CH₂(CH₂)₃CH₃, alpha product SCH(<u>CH₃</u>)CH₂(CH₂)₂CH₃), 0.89–0.86 (m, 12H, chain end -CH₃), 0.76–0.73 (m, 16H, Si<u>CH₂</u>CH₂CH₂CH₂S) ²⁹Si NMR (79,5 MHz, CDCl3): δ (ppm) = -67.05, -67.18 (Si-O-Si) MALDI-TOF MS: [M] + Na⁺: 1375.3333 (measured), 1375.3339 (calculated); [M] + H[•] + Na⁺: 1376.3370 (measured), 1376.3417 (calculated)

SSQ-4SH-4OCT





¹H NMR (400 MHz, CDCl₃): δ(ppm) = 2.71–2.64 (m, 4H, alpha product SCH(CH₃)CH₂(CH₂)₄CH₃), 2.57–2.49 (m, 24H, -CH₂SCH₂-), 1.74–1.65 (m, 16H, SiCH₂CH₂CH₂S), 1.61–1.53 (m, 8H, SCH₂CH₂(CH₂)₅CH₃), alpha product SCH(CH₃)CH₂(CH₂)₄CH₃), 1.39–1.35 (m, 4H, SH), 1.30–1.25 (m, 40H, SCH₂CH₂(CH₂)₅CH₃, alpha product SCH(CH₃)CH₂(CH₂)₄CH₃), 0.89–0.86 (m, 12H, chain end -CH₃), 0.77–0.73 (m, 16H, SiCH₂CH₂CH₂S)

²⁹Si NMR (79,5 MHz, CDCl₃): δ (ppm) = -67.06 (cage)

MALDI-TOF MS: [M] + Na⁺: 1487.436 (measured), 1487.459 (calculated);

[M] + H[•] + Na⁺: 1488.439 (measured), 1488.467 (calculated)

SSQ-4SH-4OD



Chemical Formula: C₉₆H₂₀₀O₁₂S₈Si₈

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 2.54–2.47 (m, 24H, -<u>CH₂SCH₂-)</u>, 1.73–1.68 (m, 16H, SiCH₂<u>CH₂CH₂CH₂S</u>), 1.60–1.55 (m, 8H, SCH₂<u>CH₂(CH₂)₁₅CH₃)</u>, 1.40–1.37 (m, 4H, <u>SH</u>), 1.34–1.25 (m, 120H, SCH₂CH₂(<u>CH₂)₁₅CH₃</u>, 0.90–0.86 (m, 12H, chain end -CH₃), 0.77–0.72 (m, 16H, SiCH₂CH₂CH₂CH₂S)

²⁹Si NMR (79,5 MHz, CDCl₃): δ (ppm) = -67.11 (cage) MALDI-TOF MS: [M] + H[•] + Na⁺: 2049.099 (measured), 2049.093 (calculated);

[M] + Na⁺: 2048.103 (measured), 2048.086 (calculated)

SSQ-4SH-4OFP





¹H NMR (400 MHz, CDCl₃): δ (ppm) = 6.05 (tt, J1 = 52.0 Hz, J2 = 5.5 Hz, 4H, -CF₂H), 3.91 (t, 8H, O-<u>CH₂-CF₂)</u>, 3.67 (t, 8H, O-<u>CH₂-CH₂-CH₂-S</u>), 2.61–2.51 (m, 24H, O-CH₂-CH₂-<u>CH₂-S</u>, S-<u>CH₂-CH₂-CH₂-S</u>), 1.91–1.82 (m, 8H, O-CH₂-<u>CH₂-CH₂-S</u>), 1.73–1.70 (m, 16H, S-CH₂-<u>CH₂-CH₂-S</u>), 1.44–1.38 (m, 4H, <u>SH</u>), 0.75 (s, 16H, S-CH₂-CH₂-S)) ²⁹Si NMR (79,5 MHz, CDCl₃): δ (ppm) = -64.56 (Si-OH), -65.86-(-67.14) (Si-O-Si) MALDI-TOF-MS



[M] + Na⁺: 1885.1563 (measured), 1885.103162 (calculated) [M] + H[•] + Na⁺: 1886.1454 (measured), 1886.110962 (calculated)

SSQ-4SH-4TMOS



Chemical Formula: C44H104O24S8Si12

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 3.57 (s, 36H, OMe), 2.63–2.52 (m, 24H, SiCH₂CH₂CH₂SCH₂CH₂Si(OMe)₃), 1.70–1.63 (m, 16H, SiCH₂CH₂CH₂SCH₂CH₂Si(OMe)₃), 1.40–1.37 (m, 4H, SH), 1.00–0.97 (m, 8H, SiCH₂CH₂CH₂SCH₂CH₂Si(OMe)₃), 0.75–0.72 (m, 16H, SiCH₂CH₂CH₂CH₂CH₂SCH₂CH₂Si(OMe)₃)

²⁹Si NMR (79,5 MHz, CDCl₃): δ (ppm) = -44.72 (Si(OMe)₃), -67.14 (cage) MALDI-TOF-MS: [M] + H[•] + Na⁺: 1632.116 (measured), 1632.187 (calculated)

SSQ-4SH-4AGE



¹H NMR (400 MHz, CDCl₃): δ (ppm) = 3.75-3.71 (m, 4H, position 3), 3.61-3.56 (m, 8H, position 4), 3.39-3.36 (m, 4H, position 3), 3.15-3.12 (m, 4H, position 2), 2.81-2.79 (m, 4H, position 1), 2.61-2.59 (m, 4H, position 1), 2.54-2.49 (m, 24H, -<u>CH₂SCH₂</u>), 1.89-1.84 (m, 8H, position 5), 1.74-1.66 (m, 24H, SiCH₂<u>CH₂</u>CH₂S, and position 6), 1.39-1.35 (m, 4H, SH), 0.77-0.73 (m, 16H, SiCH₂CH₂CH₂S)

²⁹Si NMR (79,5 MHz, CDCl₃): δ (ppm) = -67.11 (cage)

MALDI-TOF-MS: [M] + H[•] + Na⁺: 1496.226 (measured), 1496.237 (calculated)

SSQ-4SH-4STYR



Chemical Formula: C₅₆H₈₈O₁₂S₈Si₈

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.28–7.14 (m, 20H, Ph), 2.87–2.83 (m, 8H, S<u>CH₂CH₂Ar</u>), 2.75–2.70 (m, 8H, SCH₂<u>CH₂Ar</u>), 2.55–2.48 (m, 16H, SiCH₂CH₂CH₂S), 1.72–1.66 (m, 16H, SiCH₂<u>CH₂CH₂S</u>), 1.40–1.34 (m, 4H, SH), 0.76–0.73 (m, 16H, Si<u>CH₂CH₂CH₂CH₂S</u>) ²⁹Si NMR (79,5 MHz, CDCl₃): δ (ppm) = -67.01 (cage) MALDI-TOF-MS: [M] + H[•] + Na⁺: 1456.220 (measured), 1456.217 (calculated)

2.5. General Procedure for Thiol-Ene Tests with Octa(3-thiopropyl)silsesquioxane in the Presence of DMPA

The thiol-ene reactions were carried out under an air atmosphere in vials equipped with a magnetic stirrer. A total of 0.04921 mmol (50 mg) of crystalline SSQ-8SH, 1 equivalent of olefin per -SH group (4 groups), 3 mL of DCM, and 1 wt.% relative to the SSQ-8SH weight were placed in the vials. The mixture was vigorously stirred for 5 min under 365 nm UV radiation. Then, the solvent was evaporated under a vacuum to dry. The progress of the reaction was controlled by ¹H NMR.

2.6. General Procedure for Preparation Composites

The thiol-ene reactions were carried out under an air atmosphere in vials equipped with a magnetic stirrer. SSQ-4SH-4R, resin, 3 mL of toluene, and 1 wt.% DMPA relative to the resin/SSQ-4SH-4R weight were placed in the vials. The mixture was vigorously stirred for 5 min. Then, the mixture was placed on a Petri dish and exposed to UV radiation with a wavelength of λ = 365 nm for one hour. Coatings with different SSQ-4SH-4R concentrations were obtained (Table 1).

Modifier Content [%]	SSQ-4SH-4R [g]	Resin [g]	Initiator DMPA [g]
Reference	0	6.00	0.06
0.5	0.03	5.97	0.06
1.0	0.06	5.93	0.06
1.5	0.09	5.91	0.06
2.0	0.12	5.88	0.06
2.5	0.15	5.85	0.06
5.0	0.30	5.70	0.06
10	0.60	5.40	0.06
15	0.90	5.10	0.06
20	1.20	4.80	0.06
25	1.50	4.50	0.06
50	3.00	3.00	0.06

Table 1. Composite systems.

3. Results

3.1. Synthesis and Analysis of Derivatives

The functionalization of octa(3-thiopropyl)silsesquioxane was carried out via the radical route, both with a temperature-activated initiator (AIBN) and a photoinitiator (DMPA). A crystalline product with a defined cage structure and an oil product, which is a mixture of condensed and incompletely condensed silanols, were used for the thiolene reaction. Both products of octa(3-thiopropyl)silsesquioxane crystalline and oil were obtained according to our previous work [44] (Figure 3). In accordance with the current trend focused on green chemistry, the oil product, which is a by-product of the reaction, has also been functionalized. The use of both AIBN and DMPA and two forms of (3-thiopropyl)trimethoxy silane condensation products allowed to determine the influence of the initiator and the SSQ-8SH form on the course of the reaction.

According to literature data, the thiol-ene reaction mechanism starts with the generation of radicals. AIBN generates one 2-cyano-2-propyl radical (NC(CH₃)₂C^{\bullet}), while the initiator DMPA produces a stable benzoyl radical ($C_6H_5CO^{\bullet}$) and an unstable dimethoxybenzyl radical (Figure 2). The instability of the dimethoxybenzyl radical causes its further decomposition, resulting in methyl benzoate and the methyl radical (CH₃•). Both the benzoyl and methyl radicals can participate in the thiol-ene reaction [18]. In the first stage of the study, we prepared partially substituted SSQ-8SH derivatives using the AIBNinitiated reaction, following the procedure outlined in our first paper [44]. Reactions were carried out in toluene at 65 °C under an inert gas flow (Argon) for 24 h, then the products were evaporated on a vacuum line. Reactions with olefins containing alkyl groups differing in chain length, i.e., hexene, octene, and octadecene, both for the crystalline and oily SSQ-8SH product, proceeded with the desired complete conversion and high yield >93% as oil products and wax products for compounds functionalized with octadecyl groups. Then, vinyltrimethoxysilane (VTMOS), allyl glycidyl ether (AGE), allyl 2,2,3,3,4,4,5,5-octafluoropentylether (Allyl-OFP), allyl methacrylate (MA), and styrene (STYR) were hydrothiolated. Derivatives containing fluoroalkyl, phenylethyl groups, and vinyltrimethoxysilane (VTMOS) and allyl glycidyl ether (AGE) lead to highly viscous oils for crystalline SSQ-8SH and insoluble polymers for oily SSQ-8SH. The use of allyl methacrylate in the modification process led to the formation of insoluble cross-linked resin, regardless of the form of silsesquioxane used. Spectroscopic characterization of these derivatives was not possible. In the next step of the process, thiol-ene photoaddition was carried out with the DMPA photoinitiator, activated with UV light at a wavelength of 365 nm for 5 min. It was observed that regardless of the initiator used, crystalline and oily SSQ-8SH derivatives were obtained in an analogous form as for AIBN. Compounds formed by substituting 4HEX and 4OCT groups gave oil products, while substitution with four octadecyl groups gave wax. Substitution of SSQ-8SH by fluoroalkyl and phenylethyl groups resulted in products in the form of viscous oils. Hydrothiolation of vinyltrimethoxysilane and allyl glycidyl ether with crystalline SSQ-8SH resulted in the formation of crosslinked resin products that were insoluble and not spectroscopically characterized. For the oil derivative SSQ-8SH, during functionalization with allyl methacrylate, after about a minute of reaction, the formation of a polymer structure and gelation were noticeable. The final product was insoluble and could not be characterized spectroscopically or spectrometrically. The hydrothiolation products of vinyltrimethoxysilane and allyl glycidyl ether were viscous oils which were analyzed with NMR spectroscopy. However, the compounds spontaneously polymerized after 48 h of being left in air. This can be explained by the presence of sensitive methoxy and epoxide groups that have been partially hydrolyzed by atmospheric moisture.



Figure 3. Hydrolytic condensation of (3-thiopropyl)trimethoxy silane.

Density measurements were carried out for the physicochemical characterization of the compounds obtained via the photoaddition of SSQ-8SH oil form with various olefins, and the data are summarized in Table 2. Measurements were carried out at 25 °C. The non-functionalized SSQ-8SH has a density of 1.299 g/cm³. The addition of alkyl groups significantly decreased the density of compounds with increasing chain length (1.198 g/cm³; 1.162 g/cm³; 1.095 g/cm³ for hexene, octene, and octadecene, respectively). The higher density of SSQ-8SH oil is due to the greater number of thiol groups (SH) present in the compound, which allows for hydrogen interactions, and greater order in the structure,

resulting in greater packing and higher parameters. The addition of alkyl groups causes disorder to increase in the structures. The fluorine derivative has a higher density than oil by 0.113 g/cm³. The derivative with aromatic groups was also characterized by high density, similar to the organosilicon precursor.

Sample	Density [g/cm ³]
SSQ-8SH oil	1.299
SSQ-4SH–4HEX	1.198
SSQ-4SH-4OCT	1.162
SSQ-4SH-4OD	1.095
SSQ-4SH-4OFP	1.412
SSQ-4SH-4STYR	1.256

Table 2. Density of SSQ-8SH and derivatives.

The hydrothiolation process yielded the best results for simple olefins such as HEX, OCT, and OD. The reaction proceeded smoothly with high conversion and yield, irrespective of the substrate and initiator used. Table 3 summarizes the products obtained via thiol-ene reaction. Alkenes with an electron-rich double bond do not homopolymerize. The reaction proceeded equally for all chain lengths. A research study by Todd M. Roper et al. using real-time infrared spectroscopy (RTIR) demonstrated that 1-hexene, 1-octene, and 1-decene displayed similar reactivity with ethyl 3-mercaptopropionate [48], which was also confirmed in our research.

Table 3. Derivatives obtained via thiol-ene reaction.

Sample	Crystalline SSQ-8SH AIBN	Oil SSQ-8SH AIBN	Crystalline SSQ-8SH DMPA	Oil SSQ-8SH DMPA
SSQ-4SH-4HEX	oil	oil	oil	oil
SSQ-4SH-4OCT	oil	oil	oil	oil
SSQ-4SH-4OD	wax	wax	wax	wax
SSQ-4SH-4OFP	highly viscous oil	highly viscous oil	highly viscous oil	highly viscous oil
SSQ-4SH-4VTMOS	oil	resin/insoluble polymer	resin/insoluble polymer	resin/insoluble polymer
SSQ-4SH-4AGE	oil	resin/insoluble polymer	resin/insoluble polymer	resin/insoluble polymer
SSQ-4SH-4STYR	oil	oil	oil	oil

Hydrothiolation of allyl methacrylate with the crystalline/oil product SSQ-8SH in the presence of both AIBN and DMPA resulted in the formation of an insoluble polymer. According to literature data, non-stoichiometric polymerization occurs in thiol-acrylic systems. During the thiol-ene reaction in the presence of initiators, there is competition between the chain-growing acrylate homopolymerization and the mechanism of gradual thiol-ene growth. Not only do acrylates homopolymerize in thiol-ene reactions, but they can also detach a hydrogen from the SH group (chain transfer). The dominance of acrylate homopolymerization affects the conversion of thiol and ene functional groups and determines the final properties of the material [49]. According to the literature, methacrylic and acrylic groups exhibit strong reactivity, even in homopolymerization, without requiring harsh conditions. It has been suggested that a reaction can occur without an initiator under the influence of UV light [50]. Thiol-ene synthesis was carried out between octa(3-thiopropyl)silsesquioxane (oil) and allyl methacrylate. The mixture was vigorously stirred for 5 min under 365 nm UV radiation. The compound was allowed to evaporate. An insoluble polymer was obtained which could not be characterized spectroscopically. Crosslinking with allyl methacrylate is inevitable already in the early stages of the reaction [51]. In order to determine the influence of the different reaction conditions, thiol-ene tests were carried out both in air and in an inert gas atmosphere (Ar). Based on the NMR analysis, no effect of oxygen on the reaction was observed for simple olefins with alkyl groups (hexene, octene, and octadecene), as well as for styrene or allyl octafluoropentylether. Oxygen in thiol-ene reactions is not an inhibitor as in the case of acrylic polymerization [49]. However, in the case of vinyltrimethoxysilane and allyl glycidyl ether, a significant effect of the reaction atmosphere on the structure of the final product was noted. These olefins are sensitive to moisture in the air and are subject to partially hydrolysis after 48 h. Due to the presence of alkoxy and oxirane groups, both derivatives are sensitive to moisture in the air, under the influence of which they may undergo partial hydrolysis. Therefore, the desired derivatives with these functional groups were obtained via reaction carried out in an argon flow. DMPA is superior to AIBN in terms of reaction time (5 min vs. 24 h). The reaction proceeds without heating and allows for high conversions of substrates and yields.

3.2. Thermogravimetric Analysis

The analysis of thermal stability and decomposition of the compounds under the influence of TGA temperature was carried out for the SSQ-8SH precursor in oil form and for functionalized derivatives obtained via photoaddition in the presence of a DMPA photoinitiator. Measurements were carried out in the temperature range of 30–950 °C in an inert atmosphere with a 10 °C/min heating rate. Figure 4 show the mass change and DTG curves. Determining the mechanism of thermal degradation of silsesquioxanes may be difficult due to the complex structures of the compounds [52,53]. Thermal measurements allow for estimating the influence of functional groups on the thermal stability of compounds. Figure 4 schematically shows the individual stages of the decomposition of compound is thermally stable and does not decompose. Above 270 °C, the first stage of decomposition begins, in which hydrogen sulfide gas is released, for which the temperature at the maximum rate of decomposition is 372.8 °C. In the next step, the alkyl groups are decomposed. Above 650 °C, the residual mass is silica and coke.



Figure 4. Scheme of the decomposition of SSQ organosilicon compounds based on SSQ-8SH [53].

By functionalizing with various groups, the course of thermal decomposition of compounds can be altered. Figure 5 displays the mass change and DTG of SSQ-8SH modified with alkyl groups containing fluorine atoms or aromatic groups. The residual mass values show a significant difference, depending on the mass of the functional group content relative to the total mass of the compound. This is demonstrated for different

chain lengths of the alkyl groups, as residual mass increases with shorter alkyl chains. Based on the 1% weight loss, possible degradation pathways of functionalized compounds were estimated, and it was observed that the most stable compounds are SSQ-4SH-4OCT, SSQ-4SH-4OFP, and SSQ-4SH-4HEX, with temperatures at 1% weight loss of 295.1 °C, 288.5 °C, and 275.3 °C, respectively. The individual stages of decomposition depend on the breaking of bonds between Si-C, C-C, and S-C. For modified compounds, the first decomposition involves the release of H₂S and the formation of volatile decomposition products of functional groups. The DTG curve for the derivative with aromatic groups indicates that the elimination of benzyl radical and H_2S can be observed at the beginning, due to the presence of two peaks. The second stage of decomposition, in the temperature range of 400–600 °C for functionalized compounds, is associated with the release of volatile products derived from propyl groups in the organosilicon precursor, and the residual mass is silica and coke. The thermogravimetric analysis of samples functionalized with vinyltrimethoxysilane, allyl glycidyl ether, and allyl methacrylate, which resulted in a resin-like final product, is shown in Figure 6. The measurements indicate that the temperatures at 1% and 5% weight loss are lower than in other functionalized compounds and in the precursor. Table 4 summarizes the results of the thermogravimetric analysis of new derivatives.



Figure 5. Mass change and DTG curves of functionalized SSQ-8SH.



Figure 6. Mass change and DTG curves of resin-like final product.

3.3. Contact Angle Analysis

The contact angle analysis was performed for products obtained via photoaddition of oil SSQ-8SH using the dip-coating method. In order to analyze the contact angle,

5% solutions of modifiers in dichloromethane were prepared. Microscope slides were immersed in the solutions, and then the slides coated with the solutions were left to evaporate the solvent in the air. The measurement of the contact angle was carried out. For the sulfur precursor and the products obtained, three independent measurements were performed (Table 5).

N ₂	1% Mass Loss [°C]	5% Mass Loss [°C]	Onset Temperature [°C]	Temperature at the Maximum Rate of Mass Loss [°C]	Onset Temperature [°C]	Temperature at the Maximum Rate of Mass Loss [°C]
SSQ-8SH oil	243.0	337.5	343.6	372.8	465.9	506.5
SSQ-4SH-4HEX	275.3	341.9	356.2	377.2	470.6	507.6
SSQ-4SH-4OCT	295.1	340.5	355.1	347.4	471.4	512
SSQ-4SH-4OD	137.6	281.6	357.4	377.3	480.3	502.2
SSQ-4SH-4OFP	288.5	336.7	355.8	375.1	483.7	502.0
SSQ-4SH-4STYR	174.8	290.7	299.7	328.4	476.8	511.6
SSQ-4SH-4MA	123.9	251.5	352.6	372.1	480.0	487.1
SSQ-4SH-4AGE	126.1	291.9	336.5	363.5	492.5	503.5
SSQ-4SH-4TMOS	88.9	284.2	352.1	378.5	497.1	521.4

Table 4. Results of thermogravimetric analysis of new derivatives.

Table 5. The contact angle of new derivatives.

Sample	Contact Angle [°]
Reference	58.1 ± 0.5
SSQ-8SH oil	85.7 ± 1.5
SSQ-4SH-4HEX	63.7 ± 1.0
SSQ-4SH-4OCT	69.2 ± 1.2
SSQ-4SH-4OD	96.9 ± 2.1
SSQ-4SH-4OFP	79.1 ± 1.0
SSQ-4SH-4TMOS	60.5 ± 2.4
SSQ-4SH-4AGE	98.4 ± 2.6
SSQ-4SH-4STYR	74.2 ± 1.3

The reference sample-clear microscope slide has a contact angle of 58.1°, indicating hydrophilic properties. The SSQ-8SH oil has a contact angle of 85.7°, indicating values close to hydrophobic. The alkyl, fluoroalkyl, and phenylethyl groups in SSQ-8SH result in lower contact angles of 22° (HEX), 16.5° (OCT), 6.6° (OFP), and 11.5° (STYR), respectively compared to the SSQ-8SH sample. According to the literature, the alkyl and fluoroalkyl groups determine hydrophobic properties. However, after applying compounds with alkyl and fluoroalkyl groups, a smooth coating forms on the slide, which causes a decrease in the value of the contact angle. The precursor SSQ-8SH have high viscosity, but the addition of alkyl, fluoroalkyl, or aromatic groups lowers their viscosity, making them spread more easily on the slide's surface. The contact angle for the SSQ-4SH-4OD sample is 96.9° (11.2° increase compared to SSQ-8SH, 38.8° compared to reference sample) due to the length of the alkyl chains determining the hydrophobic character. In addition, this compound, after evaporation, is a wax, and its state of aggregation also causes a higher contact angle compared to liquid oils with alkyl groups, i.e., SSQ-4SH-4HEX or SSQ-4SH-4OCT. SSQ-4SH-4TMOS is characterized by a contact angle parameter of 60.5°. This is a decrease in relation to the SSQ-8SH of 25.2°. The lower contact angle is caused by the presence of methoxy groups, which have a higher affinity for water and lower the contact angle value. The highest value of the contact angle was obtained for the sample SSQ-4SH-4AGE (98.4°). The high contact angles suggesting a hydrophobic character for the obtained SSQ-8SH derivative probably indicate the formation of a gelled, polymeric structure, as described in the previous sections. The photos of the measurement are presented in Figure 7.



Figure 7. Images of water droplets.

3.4. Modification of UV-Curable Resin

Organosilicon compounds can be modifiers of plastics, including photo-curable resins. Thanks to the presence of two types of functional groups, the designed new derivatives can act as both factors interacting with the polymer matrix (the presence of reactive thiol groups enables the modification of (meth)acrylic resins via a "*click*" reaction) and as factors influencing the change of composite parameters. For this purpose, two derivatives were selected, characterized by the presence of four hydrophobic functional groups and four reactive -SH groups (SSQ-4SH-4OCT and SSQ-4SH-4OFP). A simplified scheme of the network formation between the resin and derivatives is shown in Figure 8.



Figure 8. A simplified scheme of the network formation.

A modification of the commercially available difunctional aliphatic urethane acrylate (Ebecryl) resin was carried out. Composites with concentrations of 0.5%, 1.0%, 1.5%, 2.5%, 5.0%, 10%, 15%, 20%, and 50% by weight were obtained (Figure 9). Based on the photos presented, it is evident that the composites made with Ebecryl/SSQ-4SH-4OCT show good

miscibility of both components to each other. However, when the Ebecryl/SSQ-4SH-4OFP modifier is used, visible air bubbles can be observed. This is attributed to the incompatibility between the organosilicon modifier and the resin, which is caused by the high hydrophobic nature of the fluoroalkyl groups.



Figure 9. Images of composites: (A) SSQ-4SH-4OCT/Ebecryl, (B) SSQ-4SH-4OFP/Ebecryl.

3.4.1. Thermal Analysis (TGA)

Thermal analysis (TGA) of both the reference Ebecryl resin and the composites was performed in nitrogen to determine the thermal stability of the compounds (Figures 10 and 11). Based on TGA and DTG, the temperature of 5% mass loss, onset, the temperature at the maximum rate of mass loss, and residual mass were determined (Table 6). Temperature changes ΔT between composites and unmodified resin were also determined. Figure 10 shows TGA analysis of Ebecryl/SSQ-4SH-4OCT, and Figure 11 Ebecryl/SSQ-4SH-4OFP.



Figure 10. TGA curves recorded for Ebecryl/SSQ-4SH-4OCT in nitrogen: (**A**) mass change, (**B**) ΔT for onset temperature.



Figure 11. TGA curves recorded for Ebecryl/SSQ-4SH-4OFP in nitrogen: (**A**) mass change, (**B**) ΔT for onset temperature.

	The Temperature at 5% Mass Change [°C]		t 5% Mass Onset Temperature C] [°C]		Temperature at the Maximum Rate of Mass Loss [°C]	
	N ₂	ΔT	N_2	ΔT	N ₂	ΔT
Ebecryl	290.4	-	306.0	-	345.3	-
0.5% SSQ-4SH-4OFP	297.5	7.1	321.1	15.1	358.8	13.5
1.0% SSQ-4SH-4OFP	288.0	-	318.8	12.8	351.2	5.9
1.5% SSQ-4SH-4OFP	292.1	1.7	319.2	13.2	351.8	6.5
2.5% SSQ-4SH-4OFP	283.7	-	314.7	8.7	349.1	3.8
5% SSQ-4SH-4OFP	284.0	-	313.9	7.9	350.1	4.8
10% SSQ-4SH-4OFP	285.0	-	312.8	6.8	345.6	0.3
15% SSQ-4SH-4OFP	301.7	11.3	322.7	16.7	354.4	9.1
20% SSQ-4SH-4OFP	304.2	13.8	323.9	17.9	361.7	16.4
50% SSQ-4SH-4OFP	304.4	14.0	325.2	19.2	360.2	14.9
0.5% SSQ-4SH-4OCT	273.5	-	307.0	1.0	341.1	-
1.0% SSQ-4SH-4OCT	277.4	-	310.9	4.9	341.8	-
1.5% SSQ-4SH-4OCT	278.8	-	312.9	6.9	341.3	-
2.5% SSQ-4SH-4OCT	280.7	-	312.5	6.5	341.0	-
5% SSQ-4SH-4OCT	285.1	-	316.1	10.1	348.2	2.9
10% SSQ-4SH-4OCT	291.1	0.7	318.0	12.0	348.8	3.5
15% SSQ-4SH-4OCT	285.8	-	314.7	8.7	348.1	2.8
20% SSQ-4SH-4OCT	285.7	-	314.6	8.6	348.3	3.0
50% SSQ-4SH-4OCT	306.0	15.6	317.9	11.9	353.6	8.3

Table 6. Results of thermogravimetric analysis of the modified resin.

The conducted analyses show that the addition of derivatives causes a significantly increased thermal stability of the composites. The addition of SSQ-4SH-4OCT increases the temperatures of 1% mass loss and 5% mass loss and the onset degradation start temperature. The temperature at the maximum rate of mass loss for the 50% composite is 353.6 °C, which is an increase over the reference of 8.3 °C. As a result of the *"click"* reaction between the acrylic resin and thiols group, new bonds are formed, creating a 3D polymer network. This results in the strengthening of the materials, and thus better thermal stability. An additional factor that increases $T_{1\%}$, $T_{5\%}$, and onset is the high stability of the organosilicon precursor. With the increase in SSQ-4SH-4R concentration, the increase in residual masses

is visible. Residual mass indicates silica and coke residue, which is the residue of the organosilicon compound.

The Ebecryl/SSQ-4SH-4OFP composites also had higher values of $T_{5\%}$, onset, and temperature at the maximum rate of mass loss, due to the similar chemical nature of the compounds and the ability to perform a click reaction. However, from the determined ΔT , it can be observed that the systems with the addition of SSQ-4SH-4OCT are characterized by a linear trend, while the ΔT of the Ebecryl/SSQ-4SH-4OFP composites are characterized by the spread of outcomes. This is due to the miscibility problem between SSQ-4SH-4OFP and the resin due to the lack of compatibility between the modifier and Ebecryl. This is noticeable in the pictures (Figure 9) where there are visible air bubbles in OFP composites. We presented similar studies in our patent application, where we described the effect of -SH groups on the thermal properties of photo-cured resins [54].

Microscopic Analysis

After the thermogravimetric tests, the composites were subjected to microscopic analysis. The residual mass of samples after thermal decomposition occurring up to 950 °C was observed. Figure 12 shows images of samples with 1.0% and 50% concentrations of modifiers in composites. The structure after decomposition of composites modified with SSQ-4SH-4OCT (Figure 12A,B) and SSQ-4SH-4OFP (Figure 12C,D) was observed. The residual mass is silica and coke. It is possible to form carbides (SiC), which are characterized by a vitrified structure of the material, which is especially observed in the case of the SSQ-4SH-4OFP modification. FT-IR and Raman analysis were performed to confirm the composition of the residue.



Figure 12. Micrographs of composites after thermal analysis.

FT-IR Analysis

An FT-IR spectroscopy analysis of the residual mass of the selected concentration of SSQ-4SH-4R in the resin (50 wt%) were conducted. A total of 1.5 mg of the residue with 200 mg of KBr were ground in a mortar, and measurements in transmittance mode were carried out. As shown in Figure 13, the residual mass spectra after thermal analysis revealed bands occurring at 1100–1030 cm⁻¹, indicating the presence of asymmetric Si-O-Si stretching vibrations. Additionally, bands from out of plane deformations (Si-O-Si) were responsible for the range of 450–420 cm⁻¹. The peaks at 778 cm⁻¹ are attributed to vibrations stretching the Si–C bonds, which may indicate the process of carbonization [55]. Bands in the range of 3300–3100 cm⁻¹ were also found, which are characteristic of the presence of O-H groups.





RAMAN Spectroscopy

A Raman spectroscopy analysis of the residual mass of the selected concentration of SSQ-4SH-4R in the resin (50 wt%) was conducted (Figure 14). Raman measurements were performed with integration of 5000 ms. The spectra shown are the average of three scans. The Raman spectra showed two obvious characteristic peaks of D and G bands, corresponding to the typical amorphous carbon [56]. The G band (narrow) in the range of 1590–1600 cm⁻¹ corresponds to the in-plane stretching vibration E_{2g} mode of sp² carbon atoms. Also, in two cases, the D band (breathing mode) in the range of 1318–1345 cm⁻¹ can be observed, which is characteristic of disordered carbon [57,58].



Figure 14. Raman spectra of residual mass.

3.4.2. Contact Angle (WCA)

The contact angle analysis was carried out for the reference sample and composites (Figure 15). The derivatives were characterized by the presence of hydrophobic groups (octyl, fluoroalkyl). The modification of Ebecryl with the SSQ-4SH-4OCT derivative resulted in an increase in the value of the contact angle. This value changed linearly with increasing concentration of the modifier in the sample. The reference has an angle of 75.5°, while the composite 50% SSQ-4SH-4OCT has an angle of 100.1°, which is an increase of 24.6°. The added SSQ-4SH-4OFP also caused an increase in the value of the contact angle, but there are clear deviations and no linear trend. The SSQ-4SH-4OCT derivative was dispersed in Ebecryl with ease, while the fluoro groups in the compound caused uneven mixing in the resin, also resulting in air bubbles. Large deviations for SSQ-4SH-4OFP composites are

caused by poor dispersion of the modifier in the material. The presence of reactive -SH groups allows for the formation of a network with the resin, while hydrophobic functional groups significantly affect the surface properties of materials.



Figure 15. Results of contact angle analysis.

4. Conclusions

The presented paper showcases the synthesis of new SSQ-8SH derivatives with attached alkyl groups of various chain lengths (hexyl, octyl, and octadecyl), (trimethoxysilyl)ethyl, 3-glycidoxypropyl, phenylethyl, and fluoroalkyl groups. These products were characterized spectroscopically (NMR) and spectrometrically (MALDI-TOS-MS). The effects of the initiator (thermal and photoinitiator) and the form of SSQ-8SH on the reaction course were compared. The tests conducted revealed that the reaction in the presence of a photoinitiator was more effective in terms of time and conditions (no heating). The products substituted with alkyl, fluoroalkyl, and phenylethyl groups were obtained with high conversions and yields towards the desired compounds. Hydrothiolation of vinyltrimethoxysilane and allyl glycidyl ether resulted in obtaining oils only by reacting with crystalline SSQ-8SH in the presence of AIBN in an inert gas atmosphere. Under other conditions, slow cross-linking occurred, resulting in insoluble polymers. Tests conducted between SSQ-8SH and allyl methacrylate resulted in insoluble polymers due to the nature of the methacrylic groups. The physicochemical tests conducted confirmed the substantial impact of various functional groups on the organization in the structure (decrease in density for derivatives with alkyl groups), thermal stability (temperature increase for the parameter 1% mass loss by 52 °C for SSQ-SH-4OCT, 45.5 °C for SSQ-SH-4OFP, and 32 °C for SSQ-SH-4HEX), or a change in hydrophobic properties. This work presented attempts at the application of novel compounds of the silsesquioxanes (SSQs) type as additives for controlling the properties of resin. The effects of the additive molecular structure were discussed with respect to the additive-resin miscibility and the thermal and surface properties of such obtained materials. Thermal and contact angle analysis indicates the potential use of derivatives as resin modifiers.

Author Contributions: Conceptualization, R.E.P.; methodology, R.E.P., B.S. and D.P.; software, D.P.; validation, B.S., R.E.P. and D.P.; formal analysis, D.P., R.E.P. and B.S.; investigation, D.P., R.E.P. and B.S.; data curation, D.P., R.E.P. and B.S.; writing—original draft preparation, D.P., B.S. and R.E.P.; writing—review and editing, D.P., B.S. and R.E.P.; visualization, R.E.P., B.S., D.P. and B.M.; supervision, B.M. and R.E.P.; project administration, D.P. and R.E.P. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by Ministry of Science and Higher Education, Poland, no "21/529535/SPUB/SP/2022", Adam Mickiewicz University, Poznań.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

AIBN	Azobisisobutyronitrile
DMPA	2,2-dimethoxy-2-phenylacetophenone
SSQ	Silsesquioxane
HEX	Hexene
OCT	Octene
OD	Octadecene
VTMOS	Vinyltrimethoxysilane
AGE	Allyl glycidyl ether
Allyl-OFP/OFP	Allyl 2,2,3,3,4,4,5,5-octafluoropentylether
MA	Allyl methacrylate
STYR	Styrene
TGA	Thermogravimetric analysis
WCA	Water contact angle
FT-IR	Fourier-transform infrared spectroscopy

References

- 1. Posner, T. Beiträge zur Kenntniss der ungesättigten Verbindungen. II. Ueber die Addition von Mercaptanen an ungesättigte Kohlenwasserstoffe. *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 646–657. [CrossRef]
- 2. Hoyle, C.E.; Bowman, C.N. Thiol-ene click chemistry. Angew. Chem. Int. Ed. 2010, 49, 1540–1573. [CrossRef] [PubMed]
- Przybylak, M.; Przybylska, A.; Szymańska, A.; Maciejewski, H. Superhydrophobization of cotton textiles by difunctional cyclic siloxanes via thiol-ene click reaction. *Cellulose* 2023, 30, 5419–5436. [CrossRef]
- 4. Nolan, M.D.; Scanlan, E.M. Applications of thiol-ene chemistry for peptide science. Front. Chem. 2020, 8, 583272. [CrossRef]
- 5. Rissing, C.; Son, D.Y. Application of thiol-ene chemistry to the preparation of carbosilane—thioether dendrimers. *Organometallics* **2009**, *28*, 3167–3172. [CrossRef]
- Liang, L.; Tan, W.; Dong, Y.; Gu, F.; Meng, X. Modified cotton fabric based on thiolene click reaction and its oil/water separation application. *Environ. Technol.* 2022, 43, 4137–4146. [CrossRef] [PubMed]
- Przybylak, M.; Szymańska, A.; Maciejewski, H.; Makowska, K. Durable, highly hydrophobic modification of cotton fabric with fluorine-free polysiloxanes obtained via hydrosilylation and hydrothiolation reactions. *Cellulose* 2020, 27, 8351–8367. [CrossRef]
- 8. Matsukawa, K.; Fukuda, T.; Watase, S.; Goda, H. Preparation of photo-curable thiol-ene hybrids and their application for optical materials. *J. Photopolym. Sci. Technol.* **2010**, *23*, 115–119. [CrossRef]
- Marcinkowska, A.; Gajewski, P.; Szcześniak, K.; Sadej, M.; Lewandowska, A. Ionogels obtained by thiol-ene photopolymerization—physicochemical characterization and application in electrochemical capacitors. *Molecules* 2021, 26,758. [CrossRef]
- 10. Sawicki, L.A.; Kloxin, A.M. Design of thiol–ene photoclick hydrogels using facile techniques for cell culture applications. *Biomater. Sci.* **2014**, *2*, 1612–1626. [CrossRef]
- Cabrero-Antonino, J.R.; Leyva-Perez, A.; Corma, A. Iron-Catalysed Markovnikov Hydrothiolation of Styrenes. *Adv. Synth. Catal.* 2012, 354, 678–687. [CrossRef]
- 12. Belley, M.; Zamboni, R. Addition of thiols to styrenes: Formation of benzylic thioethers. J. Org. Chem. 1989, 54, 1230–1232. [CrossRef]
- Chan, J.W.; Hoyle, C.E.; Lowe, A.B.; Bowman, M. Nucleophile-initiated thiol-Michael reactions: Effect of organocatalyst, thiol, and ene. *Macromolecules* 2010, 43, 6381–6388. [CrossRef]
- 14. Chan, J.W.; Yu, B.; Hoyle, C.E.; Lowe, A.B. Convergent synthesis of 3-arm star polymers from RAFT-prepared poly (N,N-diethylacrylamide) via a thiol–ene click reaction. *Chem. Comm.* **2008**, *40*, 4959–4961. [CrossRef] [PubMed]
- 15. Chan, J.W.; Hoyle, C.E.; Lowe, A.B. Sequential phosphine-catalyzed, nucleophilic thiol– ene/radical-mediated thiol– yne reactions and the facile orthogonal synthesis of polyfunctional materials. *J. Am. Chem. Soc.* **2009**, *131*, 5751–5753. [CrossRef]
- 16. Kakwere, H.; Perrier, S. Orthogonal "relay" reactions for designing functionalized soft nanoparticles. *J. Am. Chem. Soc.* 2009, 131, 1889–1895. [CrossRef]
- 17. Cramer, N.B.; Scott, J.P.; Bowman, C.N. Photopolymerizations of thiol- ene polymers without photoinitiators. *Macromolecules* **2002**, *35*, 5361–5365. [CrossRef]
- 18. Lowe, A.B. Thiol-ene "click" reactions and recent applications in polymer and materials synthesis. *Polym. Chem.* **2010**, *1*, 17–36. [CrossRef]
- 19. Sinha, A.K.; Equbal, D. Thiol– Ene Reaction: Synthetic Aspects and Mechanistic Studies of an Anti-Markovnikov-Selective Hydrothiolation of Olefins. *Asian J. Org. Chem.* **2019**, *8*, 32–47. [CrossRef]
- Degirmenci, I. Effect of Initiator Structure on Thiol-Ene Polymerization: A DFT Study. Macromol. Theory Simul. 2022, 31, 2100040. [CrossRef]
- 21. Mackey, N.M.; Confait, B.S.; Wynne, J.H.; Buchanan, J.P. Preparation of novel hydrolyzing urethane modified thiol-ene networks. *Polymers* **2011**, *3*, 1849–1865. [CrossRef]

- 22. Fina, A.; Tabuani, D.; Carniato, F.; Frache, A.; Boccaleri, E.; Camino, G. Polyhedral oligomeric silsesquioxanes (POSS) thermal degradation. *Thermochim. Acta* 2006, 440, 36–42. [CrossRef]
- Groch, P.; Dziubek, K.; Czaja, K. Coordination polymerization of alkenylsilsesquioxanes and their copolymerization with olefins or styrene/Polimeryzacja koordynacyjna alkenylosilseskwioksanow i ich kopolimeryzacja z olefinami lub styrenem. *Polimery* 2015, 60, 28–298. [CrossRef]
- Kickelbick, G. Silsesquioxanes. In Functional Molecular Silicon Compounds I. Structure and Bonding; Scheschkewitz, D., Ed.; Springer: Cham, Switzerland, 2013; Volume 155, pp. 1–28.
- Kannan, R.Y.; Salacinski, H.J.; Butler, P.E.; Seifalian, A.M. Polyhedral oligomeric silsesquioxane nanocomposites: The next generation material for biomedical applications. *Acc. Chem. Res.* 2005, *38*, 879–884. [CrossRef]
- 26. Mohamed, M.G.; Kuo, S.W. Functional polyimide/polyhedral oligomeric silsesquioxane nanocomposites. *Polymers* **2018**, *11*, 26. [CrossRef]
- Li, G.Z.; Wang, L.; Toghiani, H.; Daulton, T.L.; Koyama, K.; Pittman, C.U. Viscoelastic and mechanical properties of epoxy/multifunctional polyhedral oligomeric silsesquioxane nanocomposites and epoxy/ladderlike polyphenylsilsesquioxane blends. *Macromolecules* 2001, 34, 8686–8693. [CrossRef]
- Lee, K.S.; Chang, Y.W. Thermal and mechanical properties of poly (ε-caprolactone)/polyhedral oligomeric silsesquioxane nanocomposites. *Polym. Int.* 2013, 62, 64–70. [CrossRef]
- 29. Sztorch, B.; Brząkalski, D.; Głowacka, J.; Pakuła, D.; Frydrych, M.; Przekop, R.E. Trimming flow, plasticity, and mechanical properties by cubic silsesquioxane chemistry. *Sci. Rep.* **2023**, *13*, 14156. [CrossRef]
- Sztorch, B.; Pakuła, D.; Kustosz, M.; Romanczuk-Ruszuk, E.; Gabriel, E.; Przekop, R.E. The Influence of Organofunctional Substituents of Spherosilicates on the Functional Properties of PLA/TiO₂ Composites Used in 3D Printing (FDM/FFF). *Polymers* 2022, 14, 5493. [CrossRef]
- 31. Alves, F.; Nischang, I. Tailor-made hybrid organic–inorganic porous materials based on polyhedral oligomeric silsesquioxanes (POSS) by the step-growth mechanism of thiol-ene "click" chemistry. *Chem. Eur. J.* **2013**, *19*, 17310–17313. [CrossRef]
- Daga, V.K.; Anderson, E.R.; Gido, S.P.; Watkins, J.J. Hydrogen bond assisted assembly of well-ordered polyhedral oligomeric silsesquioxane–block copolymer composites. *Macromolecules* 2011, 44, 6793–6799. [CrossRef]
- Hartmann-Thompson, C. Polyhedral oligomeric silsesquioxanes in electronics and energy applications. In Applications of Polyhedral Oligomeric Silsesquioxanes; Springer: Dordrecht, The Netherlands, 2010; pp. 247–325.
- Bivona, L.A.; Fichera, O.; Fusaro, L.; Giacalone, F.; Buaki-Sogo, M.; Gruttadauria, M.; Aprile, C. A polyhedral oligomeric silsesquioxane-based catalyst for the efficient synthesis of cyclic carbonates. *Catal. Sci. Technol.* 2015, *5*, 5000–5007. [CrossRef]
- Li, X.; Du, Y.; Dai, J.; Wang, X.; Yang, P. Metal nanoparticles stabilized by cubic silsesquioxanes for catalytic hydrogenations. *Catal.* Lett. 2007, 118, 151–158. [CrossRef]
- 36. Jash, P.; Wilkie, C.A. Effects of surfactants on the thermal and fire properties of poly (methyl methacrylate)/clay nanocomposites. *Polym. Degrad. Stab.* **2005**, *88*, 401–406. [CrossRef]
- Cazacu, M.; Bargan, A.; Balan, M.; Vornicu, N.; Varganici, C.D.; Shova, S. Full functionalized silica nanostructure with well-defined size and functionality: Octakis (3-mercaptopropyl) octasilsesquioxane. *J. Organomet. Chem.* 2015, 799, 195–200.
- Sierke, J.K.; Ellis, A.V. High purity synthesis of a polyhedral oligomeric silsesquioxane modified with an antibacterial. *Inorg. Chem. Commun.* 2015, 60, 41–43. [CrossRef]
- 39. Dai, J.; Zhang, T.; Zhao, H.; Fei, T. Preparation of organic-inorganic hybrid polymers and their humidity sensing properties. *SensActuators B Chem.* **2017**, 242, 1108–1114. [CrossRef]
- 40. Gan, Y.; Jiang, X.; Yin, J. Self-wrinkling patterned surface of photocuring coating induced by the fluorinated POSS containing thiol groups (F-POSS-SH) as the reactive nanoadditive. *Macromolecules* **2012**, *45*, 7520–7526. [CrossRef]
- 41. Lee, A.S.; Jo, Y.Y.; Choi, S.S.; Baek, K.Y.; Hwang, S.S. Thermal, Mechanical, and Photophysical Properties of Carbazole-Substituted POSS and Ladder Polysilsesquioxane. *J. Nanosci. Nanotechnol.* **2017**, *17*, 5562–5565. [CrossRef]
- 42. Li, W.; Feng, S. New sensors for the detection of picric acid: Ionic liquids based on polyhedral oligomeric silsesquioxanes prepared via a thiol-ene click reaction. *J. Mol. Liq.* **2018**, *265*, *269–275*. [CrossRef]
- 43. Liu, L.; Lee, S.J.; Lee, M.E.; Kang, P.; Choi, M.G. Syntheses of phosphorylcholine-substituted silsesquioxanes via thiol-ene 'click'reaction. *Tetrahedron Lett.* 2015, *56*, 1562–1565. [CrossRef]
- Pakuła, D.; Przekop, R.E.; Brząkalski, D.; Frydrych, M.; Sztorch, B.; Marciniec, B. Sulfur-Containing Silsesquioxane Derivatives Obtained by the Thiol-ene Reaction: Synthesis and Thermal Degradation. *ChemPlusChem* 2022, *87*, e202200099. [CrossRef] [PubMed]
- Szymańska, A.; Przybylak, M.; Maciejewski, H.; Przybylska, A. Thiol-ene chemistry as an effective tool for hydrophobization of cotton fabrics. *Cellulose* 2022, 29, 1231–1247. [CrossRef]
- Maciejewski, H.; Karasiewicz, J.; Marciniec, B. Efektywna synteza fluorofunkcyjnych (poli)siloksanów. *Polimery* 2012, 57, 449–456. [CrossRef]
- 47. Feher, F.J.; Wyndham, K.D.; Soulivong, D.; Nguyen, F. Syntheses of highly functionalized cube-octameric polyhedral oligosilsesquioxanes (R₈Si₈O₁₂). *J. Chem. Soc. Dalton Trans.* **1999**, *19*, 1491–1498. [CrossRef]
- Roper, T.M.; Chandler, C.M.; Guymon, C.A.; Hoyle, C.E.; Jönsson, E.S. Structural influence of model ene reactivity in photoinduced thiol-ene polymerization of multifunctional alkenes. In Proceedings of the Technical Conference Proceedings-UV & EB Technology Expo & Conference, Charlotte, NC, USA, 2–4 May 2004; pp. 242–251.

- Cramer, N.B.; Bowman, C.N. Kinetics of thiol–ene and thiol–acrylate photopolymerizations with real-time fourier transform infrared. J. Polym. Sci. Part. A Polym. Chem. 2001, 39, 3311–3319. [CrossRef]
- 50. Molina-Gutiérrez, S.; Dalle Vacche, S.; Vitale, A.; Ladmiral, V.; Caillol, S.; Bongiovanni, R.; Lacroix-Desmazes, P. Photoinduced polymerization of eugenol-derived methacrylates. *Molecules* **2020**, *25*, 3444. [CrossRef] [PubMed]
- Nagelsdiek, R.; Mennicken, M.; Maier, B.; Keul, H.; Höcker, H. Synthesis of polymers containing cross-linkable groups by atom transfer radical polymerization: Poly (allyl methacrylate) and copolymers of allyl methacrylate and styrene. *Macromolecules* 2004, 37, 8923–8932. [CrossRef]
- 52. Frydrych, M.; Pakuła, D.; Sztorch, B.; Brząkalski, D.; Przekop, R.E.; Marciniec, B. Novel Silsesquioxane-Derived Boronate Esters—Synthesis and Thermal Properties. *Molecules* **2021**, *26*, 4107. [CrossRef]
- 53. Frydrych, M.; Sztorch, B.; Przekop, R.E.; Marciniec, B. New Ethynylphenylborasilsesquioxanes—Their Reactivity and Behavior during Thermal Decomposition. *Int. J. Mol. Sci.* 2023, 24, 13960. [CrossRef]
- Pakuła, D.; Przekop, R.E.; Sztorch, B.; Marciniec, B. Sposób Otrzymywania Modyfikowanych Żywic fotoutwardzalnych Okta(3-Tiopropylosilseskwioksanem) o Znacznie Podwyższonej Stabilności Termicznej. Poland Patent Application P.443618, 28 January 2023.
- 55. Sun, Z.G.; Wang, S.J.; Qiao, X.J.; Li, Y.; Zheng, W.H.; Bai, P.Y. Synthesis and microwave absorbing properties of SiC nanowires. *Appl. Phys. A* **2018**, *124*, 802. [CrossRef]
- Autthawong, T.; Namsar, O.; Yu, A.; Sarakonsri, T. Cost-effective production of SiO2/C and Si/C composites derived from rice husk for advanced lithium-ion battery anodes. J. Mater. Sci. Mater. Electron. 2020, 31, 9126–9132. [CrossRef]
- Pan, J.; Ren, J.; Xie, Y.; Wei, X.; Guan, Y.; Yan, X.; Tang, H.; Cheng, X. Porous SiOC composites fabricated from preceramic polymers and wood powders for efficient dye adsorption and removal. *Res. Chem. Intermed.* 2017, 43, 3813–3832. [CrossRef]
- Macias-Ferrer, D.; Melo-Banda, J.A.; Silva-Rodrigo, R.; Lam-Maldonado, M.; Páramo-García, U.; Meraz-Melo, M.A. Comparative study between removers agents of silicon into the synthesis of micro/nano-structured pyrolytic carbon from refined sugar. *Int. J. Sci. Res. Manag.* 2018, 5, 102–111.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.