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REVIEW ARTICLE

Direct Comparison between Ring-Opening Polymerization and Hydrolysis-Condensation Methods in the Synthesis of Polydimethylsiloxane as a Vitreous Substitute: A Systematic Literature Review

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Abstract

Polydimethylsiloxane (PDMS) is a polymer with outstanding biocompatibility, chemical stability, gas permeability, and optical clarity properties. It is suitable for various applications, including as a vitreous substitute in retinal surgery. PDMS provides optical stability and transparency, essential for maintaining adhesion between the retina and the retinal pigment epithelium. The main methods for synthesizing PDMS are ring-opening polymerization (ROP) and hydrolysis-condensation, both of which produce PDMS with a wide range of properties that can be tailored by adjusting the synthesis parameters. While ROP is typically performed with cyclic siloxanes such as octamethylcyclotetrasiloxane (D4), hydrolysis-condensation uses precursors such as dichlorodimethylsilane (DCDMS). This study compares the ROP and hydrolysis-condensation methods for PDMS synthesis, focusing on their effectiveness in achieving a specific viscosity range, a key parameter for vitreous replacement applications. The effectiveness of each method in achieving specific viscosity ranges for vitreous substitute applications is compared. The results indicate that ROP requires only 1 synthesis step and operates at higher temperatures (150 - 200 °C), yielding PDMS with viscosities ranging from 0.58 to 9.36 Pa·s, influenced by factors such as KOH concentration, reaction time, and D4 purity. In contrast, hydrolysis-condensation involves a 2-step process with viscosities between 0.57 and 4.49 Pa·s, affected by more complex parameters, including the DCDMS:DCM volume ratio, reaction time, and temperature during hydrolysis. Both methods achieved close refractive index values (1.3989 - 1.4048), although the surface tension varied with sample viscosity (19 - 23 mN/m). Comparative analysis reveals that although ROP is more suitable for producing high-purity PDMS efficiently. These findings contribute to understanding PDMS synthesis methods and their implications for vitreous substitute applications. Recommendations for future research on this topic include the need to conduct further biocompatibility tests such as *in vivo* tests and stability tests of PDMS samples.

Keywords: Dichlorodimethylsilane, Hydrolysis-condensation, Octamethylcyclotetrasiloxane, Polydimethylsiloxane, Ring-opening polymerization, Synthesis, Vitreous substitute

Introduction

Polydimethylsiloxane (PDMS), an organosiloxane telechelic compound, with a -[R_2Si-O]- group where R is an organic side chain. It is an elastomeric polymer with interesting properties, such as excellent bio-degeneration, biocompatibility, chemical stability, gas permeability, mechanical properties, and optical transparency. Therefore, it is a superior material and has many applications. One of the uses of this material is as a vitreous substitute [1-4].

A vitreous substitute is an artificial fluid that replaces the vitreous humor in retinal surgery to treat retinal detachment [5-7]. The ideal characteristics that a vitreous substitute must have include imitating native vitreous, having similar viscoelastic properties, being clear and transparent, being long-lasting, having a refractive index and density similar to vitreous humor (1.3345 - 1.3348 and 1.0053 - 1.008 g/cm^3), being biologically and chemically inert, and not causing toxic reactions [8,9]. Vitreous substitutes must resemble the vitreous to effectively transmit light, protect the retina from pressure and friction, and ensure biological compatibility without interfering with nutrient transfer. Therefore, PDMS is used as an intraocular tamponade in vitreoretinal surgery because it is inert, transparent, and can maintain adhesion between the retina and the retinal pigment epithelium [10,11].

Various synthetic approaches to obtain organosiloxane telechelics of a given structure are telomerization, ring-opening polymerization, hydrolysis-condensation, click reaction, etc. The most commonly used methods are ROP and hydrolysis-condensation [12,13]. ROP is a chain growth process that converts cyclic monomers into linear polymers by opening their rings [14]. Tetramethylcyclotetrasiloxane (T4), hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), and decamethylcyclopentasiloxane (D5) are materials that can be used as PDMS monomers through the ROP method. However, of these materials, the most commonly used as a PDMS monomer in vitreous substitute applications is D4. This is because D4 can be easily formed into PDMS with the desired viscosity of 1.0 - 5.5 Pa·s [15,16]. PDMS with a viscosity of 1.0 Pa·s is easier and faster to inject and dispense but has the limitation of emulsifying more quickly than higher viscosities. PDMS 5.5 Pa·s has a lower tendency to emulsify, which may result in a more prolonged tamponade effect [17]. Hydrolysis-condensation is a process that involves the reaction of a precursor (such as silane) with water, causing hydrolysis (breaking of bonds by the addition of water) followed by condensation (removal of water to form intermolecular bonds) [18,19]. Precursors that can be used in synthesizing PDMS by hydrolysis-condensation method are DCDMS, methyltrichlorosilane (MTCS), methyltriethoxysilane (MTES), methylvinilchlorosilane and methylphenylchlorosilane. DCDMS is most commonly used because it is a standard precursor for its application as a vitreous substitute [20,21].

Research on PDMS has been reviewed in several articles regarding its application. Mojsiewicz-Pie *et al.* [2] discuss the characteristics of siloxanes and their effects on human contact. Zaman *et al.* [22] present a review of the synthesis, characterization, and applications of PDMS in various copolymer forms. However, review articles that specifically compare methods for producing PDMS, especially the ROP and hydrolysis-condensation methods, are not available. This paper compares the ROP and hydrolysis-condensation methods in their applications to produce PDMS as vitreous substitutes. Comparing these 2 methods aims to determine the flexibility and effectiveness of synthesis.

Materials and methods

The databases used in the literature search were Scopus, Scientific.net, IOPscience, and MDPI, with the following search keywords: "polydimethylsiloxane" AND "vitreous" AND "substitute." Our search was limited to articles published in international journals in the last ten years written in English and accessible. Database, keywords, total articles obtained from the database, and article types are shown in **Table 1**.

Table 1 The search terms used and the total number of publications from each database.

Database	Keywords	Total articles	Article types
Scopus	"polydimethylsiloxane" AND "vitreous" AND "substitute"	11	Research article
Scientific.net		8	Research article
IOPscience		16	Book, Review article, and Research article
MDPI		2	Research article

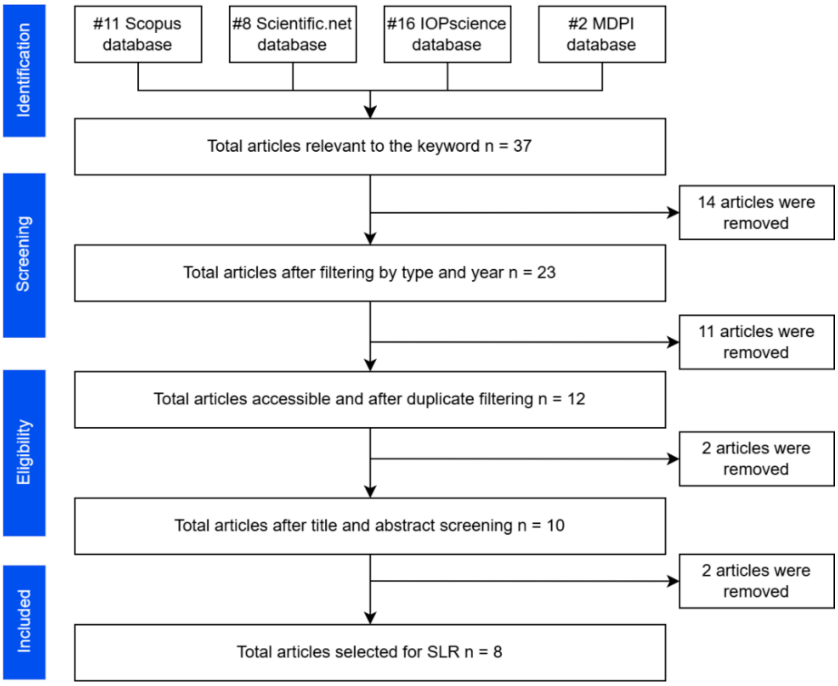

Figure 1 PRISMA for searching publication databases for systematic reviews.

Error! Reference source not found. shows the PRISMA guidelines for selection procedures. The total documents identified were 11 files from Scopus, 8 from Scientific.net, 16 from IOPscience, and 2 from MDPI. A paper screening type was used to exclude all documents other than research papers and publication years from 2014 to 2024, and 23 articles were included. A study of the characteristics of PDMS synthesized using the ROP and hydrolysis-condensation methods as a vitreous substitute is included in the criteria. The exclusion criteria applied were articles describing PDMS or PDMS in other applications. Eleven of the 23 articles were removed due to duplication and inaccessibility. Two articles were excluded because they did not discuss PDMS, and 2 articles were not included because they only discussed PDMS in general, and the data presented is incomplete. As a result, 8 full-text articles will be analyzed in this review paper, consisting of 6 articles about PDMS resulting from the ROP method and 2 articles about PDMS resulting from the hydrolysis-condensation method. **Figure 2** shows the distribution of articles on Polydimethylsiloxane (PDMS) by publication year and quartile rank.

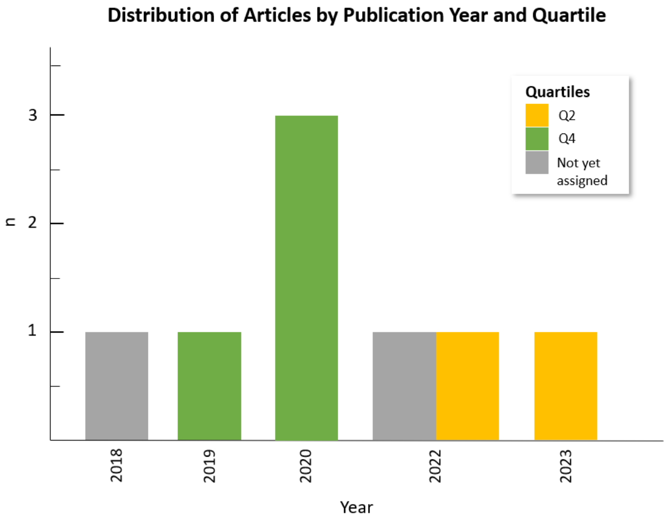

Figure 2 Illustration of distribution of articles on PDMS based on publication year and quartile rank.

Results and discussion

Synthesis of PDMS is usually carried out using the ROP method with D4 as the monomer. However, PDMS can also be synthesized using the hydrolysis-condensation method with DCDMS as the precursor. The following is a discussion of the synthesis and characteristics of each method.

Synthesis and characteristics of PDMS through the ROP method

PDMS can be synthesized through a chain-growth polymerization process called ROP. This process involves the use of an initiator and heat treatment to cleave the Si-O bond in the monomer, which allows the end of the polymer chain to act as a reactive center for the propagation process [23].

Several ROP techniques exist, namely ionic, radical, and ring-opening metathesis polymerization [24]. The most commonly used technique for synthesizing PDMS via ROP was ionic ROP. Ionic ROP is processed with a strong base or acid initiator. If a strong base is used in the polymerization process, an anionic mechanism (AROP) occurs. An acid initiator produces the cationic mechanism (CROP) [16,25,26].

AROP commonly produces PDMS because it provides better control over molecular weight and distribution, results in more consistent polymer structures, minimizes impurities and enhances chemical stability. In contrast, CROP can lead to broader molecular weight distributions due to branching and termination reactions, compromising PDMS properties [24,27-29]. The polymerization process consists of initiation, propagation, and termination. The ROP process is illustrated in **Figure 3**.

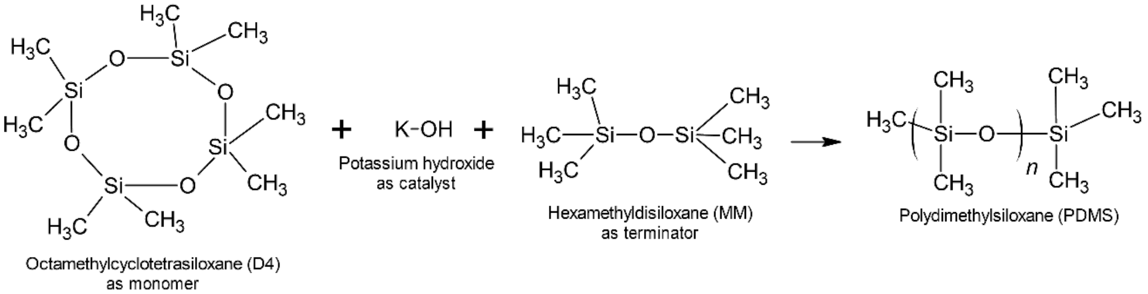

Figure 3 ROP method of D4 with the addition of KOH and hexamethyldisiloxane (MM).

In the initiation process, the monomer is treated with a strong base, which helps to form an anion that acts as the active centre for the propagation reaction. Various initiators can be used in this route, and the most commonly mentioned were alkali metal hydroxides or alkali metals (e.g. KOH and NaOH) [30]. The anion from the initiator donates a pair of electrons to one of the silicon atoms (Si) in the siloxane and forms a bond. This process causes the cyclic chain to break into a linear chain, forming siloxane bonds in the monomer ring. The oxygen molecule with a negative charge binds to the second cyclic monomer, and this process continues. In the termination process, the chain was capped to prevent further polymerization [31-33]. Materials that can be used as end-capping agents to control molecular weight in the termination process are usually disiloxanes, including tetramethylsiloxane (TMDS), MM, or divinyl tetramethyldisiloxane (DVS) [16,29].

In previous research, scientists have experimented with varying the concentration of KOH as an initiator, the reaction time, the ratio of D4 as a monomer to MM as an end-capping agent, the synthesis temperature, and the purity of D4 [23,31-35]. The objective of these variations was to achieve optimal results in the synthesis of PDMS to create an ideal substitute for vitreous. The different variations performed have yielded specific characteristics, which are explained in detail in the **Table 2**.

Based on the data presented in **Table 2**, variations in reaction parameters significantly affect polymer characteristics. Fitrilawati *et al.* [34] (S1 - S5) varied the molar concentration of KOH in the polymerization process. It turned out that the sample's viscosity would increase if the KOH concentration were increased because KOH acts as a base catalyst that accelerates the formation of siloxane bonds, which means that the viscosity increases [36-38]. However, the study showed that PDMS samples with 1.0 M KOH had a higher viscosity than those synthesized with higher KOH concentrations (2.0 and 2.5 M) [34]. The reduction in viscosity at higher KOH concentrations is most likely due to excess KOH, which induces depolymerization and chain cleavage. Thus, the KOH concentration has an optimal threshold at which the polymer chain length and viscosity begin to decrease [39]. At the same temperature and reaction time, the optimal KOH molarity as a catalyst is 1 M. The graph of viscosity changes due to KOH concentration is shown in **Figure 4**.

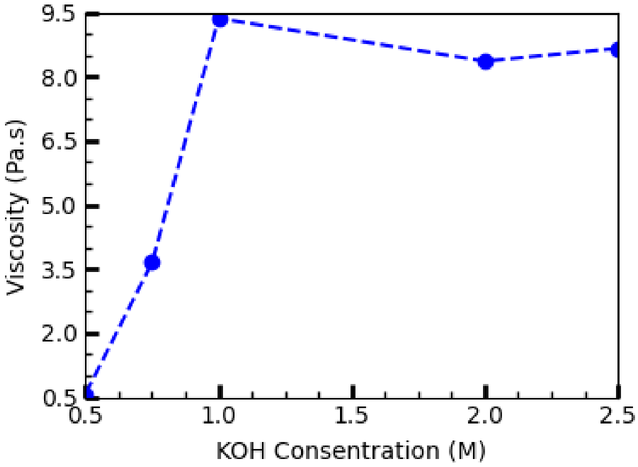

Figure 4 Graph of viscosity versus KOH concentration S1 - S5.

In addition to KOH concentration, temperature, reaction time, and D4 purity can affect viscosity. The research samples conducted by Setiadji *et al.* [32] (S16 and S17) and Waslaludin *et al.* [35] (S9 and S10) showed that the higher the temperature used, the increased viscosity. This is because temperature can affect molecular weight distribution. Temperature plays a crucial role in chemical bond formation and breaking energy dynamics. Higher temperatures provide more energy to overcome activation barriers, facilitating the formation of new bonds during polymerization. However, they can also lead to the breaking of existing bonds, which can affect the overall molecular structure [40]. The viscosity vs temperature graphs of samples S9 - S10 and S16 - S17 are shown in **Figure 5**. Therefore, paying attention to temperature parameters is necessary to obtain PDMS with the desired viscosity. Generally, a longer reaction time can elongate the polymer chain if the catalyst remains active during the reaction, thus increasing the viscosity [41]. For example, samples S6 and S8 show variations in reaction time parameters. S8 has a longer reaction time than S6, which then S8 has a higher viscosity than S6 [35]. From the description of KOH molarity, temperature, and reaction time, 200 °C is the optimal temperature because using 0.53 M KOH only requires a reaction time of 50 min. The optimal reaction time is 45 - 70 min for PDMS with low, medium, and high variations.

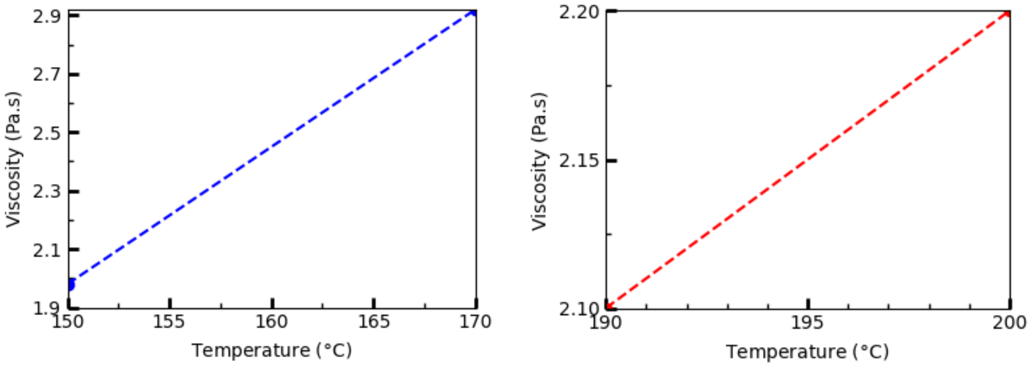

Figure 5 Graph of viscosity vs temperature (left) 0.7 M KOH and reaction time 70 min (right) 0.53 M KOH and reaction time 50 min.

Table 2 The list of sample code, synthesis parameters, and data characteristics of PDMS [23,31-35].

Sample code	KOH concentration (M)	Reaction time (min)	Synthesis temperature (°C)	D4:MM	Purity of D4 (%)	Viscosity (Pa·s)	Refractive index	Surface tension (mN/m)	Transmittance (%)	Ref
S1	0.50	45	170	13:5	-	0.58	1.3989	-	100	[34]
S2	0.75	45	170	13:5	-	3.65	1.4008	-	100	[34]
S3	1.00	45	170	13:5	-	9.36	1.4030	-	100	[34]
S4	2.00	45	170	13:5	-	8.36	1.4034	-	100	[34]
S5	2.50	45	170	13:5	-	8.66	1.4036	-	100	[34]
S6	0.58	35	170	13:5	-	1.17	1.3999	19.0	-	[35]
S7	0.75	45	170	13:5	-	3.65	1.4032	22.0	-	[35]
S8	0.58	70	170	26:10	-	1.70	1.4026	19.5	100	[35]
S9	0.75	70	170	26:10	-	2.92	1.4034	20.0	100	[35]
S10	0.75	70	150	26:10	-	1.98	1.4038	19.0	100	[35]
S11	0.58	35	170	26:10	-	1.17	1.3999	19.0	100	[33]
S12	0.58	40	170	26:10	-	3.42	1.4007	19.0	100	[33]
S13	2.00	50	190	26:10	96	1.15	1.4040	21.0	-	[23]
S14	0.60	16	150	26:10	98	1.17	1.3993	19.0	-	[23]
S15	2.00	50	190	46:10	96	1.81	1.4048	21.5	-	[23]
S16	0.53	50	200	26:10	96	2.20	1.4040	22.0	-	[32]
S17	0.53	50	190	26:10	96	2.10	1.4044	23.0	-	[32]
S18	0.71	50	190	26:10	96	2.34	1.4042	22.0	-	[32]
S19	1.06	50	190	26:10	96	2.59	1.4042	22.0	-	[32]
S20	1.42	50	190	26:10	96	1.81	1.4042	22.0	-	[32]
S21	0.60	50	180	26:10	96	0.94	1.4034	21.0	-	[31]
S22	2.00	50	190	26:10	96	1.35	1.4040	21.0	-	[31]

The next parameter is the purity of D4 used. Samples S14 and S21 use different D4 purities. With the same KOH concentration, although the reaction time and temperature differ, S14 has a higher viscosity value than S21. Even though S21 has a longer reaction time and higher temperature. D4 with higher purity extends the chain faster even though its reaction time is the shortest compared to other data [23,31].

The refractive index characteristics listed in **Table 2** show that the samples have a range of refractive indices that are close together (1.3989 - 1.4044) because they are in the same functional group [42]. The refractive index values of the samples are not identical due to the density and chain length of the samples [43]. The surface tension of the samples in **Table 2** has a value range of 19 - 23 mN/m. The surface tension is by the functional group described by other studies, around 20.4 mN/m [12,44]. The range of surface tension values obtained is by the viscosity trend of the samples, while some samples do not match the viscosity trend. Several samples have been characterized for transmittance and have a transmittance result of 100 %, meaning that all light or radiation that passes through the surface of the material is not absorbed, reflected, or scattered, or it can be said that the samples obtained are perfectly transparent [45].

Synthesis and characteristics of PDMS through hydrolysis-condensation method

Hydrolysis is the stage where the precursor reacts with water. In this case, PDMS, as a vitreous substitute, uses DCDMS as its precursor. The chlorine (or alkoxy, depending on the precursor) group is hydrolyzed, producing an -OH group attached to the silicon atom [46,47].

The hydrolysis process employs solvents because they significantly influence the reactivity of DCDMS. For example, polar solvents stabilize transition states and intermediates, facilitating the reaction. This stabilization allows for better control over the rate of hydrolysis, resulting in a more manageable reaction process. Ultimately, the use of solvents is beneficial for enhancing the reactivity, homogeneity, and stability of the final product [37,48,49]. Solvents are selected based on the general rule that states "like dissolves like," which means that polar compounds will only dissolve in polar solvents such as ethanol, methanol, butanol, and water, while nonpolar compounds can only dissolve in nonpolar solvents, such as ether, chloroform, and n-hexane [50]. PDMS synthesis generally uses dichloromethane (DCM) as a solvent in the hydrolysis process.

The following process is phase separation. Phase separation is a useful technique to separate the nonpolar phase (PDMS sample) from the residual precipitate. This process uses a separatory funnel until 2 layers of different phases are formed in the hydrolysis sample [51]. The PDMS sample is then evaporated to remove any remaining solvent or residue. After evaporation, the sample was dissolved with chloroform to separate the temporary bonds, and then the sample was washed using milli-q water until a neutral pH was obtained [52].

After hydrolysis, the -OH groups on silicon molecules can react with each other, forming silicon-oxygen bonds (Si-O-Si) and joining silicon molecules into longer chains. Chain extension to form polymers can use several methods, condensation and ROP (used if cyclic monomers are formed) [1,12,53].

The condensation method is a polymerization process formed from functional groups, such as OH, with slow and gradual reaction properties [53]. Monomers that have formed bonds with the hydroxyl (OH) functional group through hydrolysis can engage in condensation polymerization. The condensation polymerization process can be enhanced by the application of heat or the introduction of catalysts, which serve to accelerate the polymerization reaction [54]. Self-polymerization is a condensation process that utilizes the acidic or basic properties of the sample; then, the sample is left at room temperature until it reaches the desired viscosity [55].

Previous studies reported hydrolysis using DCDMS and DCM with varying volume ratios. After that, milli-q water with half of the volume of DCDMS was added [20]. Meanwhile, milli-q water in the research conducted by Fauziah *et al.* [55] was mixed with KOH. Then, the material is mixed at a specific temperature and stirring speed. The phase separation was carried out at least for 60 min. Then, the nonpolar phase was evaporated for at least 60 min at 50 °C until the remaining solvent was gone using a rotary evaporator. After the evaporation process, a clear hydrolysis gel was produced. Furthermore, purification was done to purify the sample until it reached a neutral pH of 7. The result was a pure hydrolysis gel [20].

The purified hydrolysis gel was condensed by Auliya *et al.* [20] at a temperature above 100 °C with a stirring speed of 300 rpm to obtain PDMS gel. KOH was used as a catalyst, and MM was used as a chain breaker.

The pure hydrolysis gel was mixed with 0.6 M KOH and a small amount of MM, and PDMS gel was obtained to start condensation. Meanwhile, Fauziah *et al.* [55] used the self-polymerization technique at a temperature of 15 - 20 °C for the chain extension process of the hydrolysis sample. The resulting PDMS gel was then purified to remove any residue, and pure PDMS gel was obtained. Purification was done by dissolving the sample in chloroform and washing it with milli-q water. The sample was neutralized to obtain pure PDMS gel. Chloroform was separated from the sample by evaporation, leaving pure PDMS gel [20,55]. PDMS samples can be synthesized under various conditions, such as adjusting the volume ratio between DCDMS and DCM solvents and the polymerization temperature [20,55]. The Hydrolysis-condensation process is illustrated in **Figure 6**.

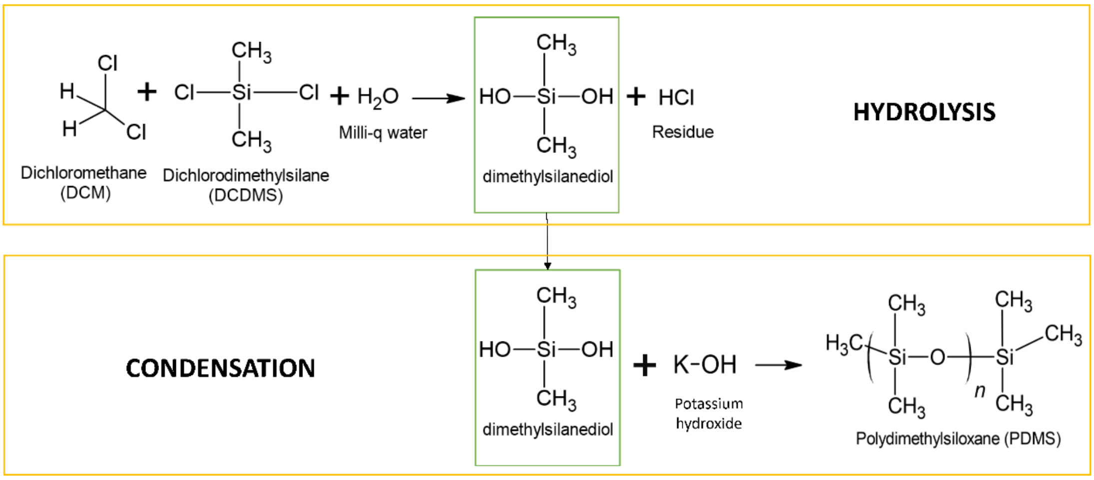

Figure 6 Hydrolysis and condensation reaction of DCDMS for PDMS synthesis.

From the description above, it can be concluded that in the hydrolysis-condensation method to produce PDMS, several synthesis parameters play an important role, as seen in **Table 3** and the characteristics of the results are seen in **Table 4**.

Table 3 Parameter of hydrolysis-condensation method.

Sample code	DCDMS:DCM	Hydrolysis		Polymerization			
		t (min)	T (°C)	KOH concentration (M)		T (°C)	t
H1	1:1	240	60	-	0.6	130	20 min
H2	1:4	240	60	-	0.6	140	20 min
H3*	1:4	120	40 - 45	0.5	-	-	48 days
H4*	1:4	120	40 - 45	0.6	-	-	63 days
H5*	1:4	120	40 - 45	1.0	-	-	18 days

*Self-polymerization

Table 4 Characteristics of PDMS from the hydrolysis-condensation method.

Sample code	Viscosity (Pa·s)	Refractive index	Surface tension (mN/m)	Transmittance (%)	Ref
H1	2.06	1.4036	21.0	100	[20]
H2	3.59	1.4034	21.0	100	[20]
H3	0.57	1.4012	19.0	-	[55]

Sample code	Viscosity (Pa·s)	Refractive index	Surface tension (mN/m)	Transmittance (%)	Ref
H4	4.49	1.4008	21.0	-	[55]
H5	1.53	1.4001	20.0	-	[55]

The viscosity presented in **Table 4** has various results. Samples H1 and H2 have viscosity values that are quite far apart. This can be concluded from the higher condensation (polymerization) temperature of H2 compared to H1 [20]. It cannot be concluded whether the comparison of the precursor and solvent volume ratio plays a role in the viscosity results of the polymer. This is because these parameters have more influence on the final results of the hydrolysis process. In contrast, the article does not present the final hydrolysis results regarding its characteristics. Samples H3, H4, and H5 have viscosities influenced by the concentration of KOH added during hydrolysis and the polymerization time [55]. There is a possibility that sample H5 may polymerize faster because it has the highest concentration of KOH. However, this cannot be concluded with certainty because each sample's self-polymerization time differs.

The refractive index characteristics of the samples in **Table 4** have a close range (1.4001 - 1.4036) because of their same functional groups. As for surface tension, the lowest viscosity has the lowest surface tension, namely in sample H3. Overall, the samples had a surface tension ranging from 19 to 21 mN/m.

The comparison of PDMS through ROP and hydrolysis-condensation method

ROP and hydrolysis-condensation methods have successfully obtained PDMS as a vitreous substitute with several viscosity ranges. However, ROP has a shorter process than hydrolysis-condensation compared to the synthesis process. ROP only requires 1 synthesis step, while hydrolysis-condensation requires 2 steps to achieve the same viscosity. Because of its lengthy process, hydrolysis-condensation requires a lot of parameter control compared to ROP.

The polymerization parameters for both processes are different. For ROP, the polymerization temperature ranges from 150 - 200 °C while the condensation process uses a temperature of 130 - 140 °C. ROP and hydrolysis-condensation require a minimum KOH concentration of 0.58 to 1 M to produce PDMS with the appropriate viscosity. The ROP method is more efficient because the total synthesis time is shorter than the hydrolysis-condensation method. The minimum synthesis time with the ROP method is 16 min, while the hydrolysis-condensation method is 260 min.

The refractive index of PDMS samples synthesized through the ROP and condensation have a range of values close to each other due to the same functional groups (1.3989 - 1.4044). The surface tension of the samples has a range of values of 19 - 23 mN/m, which is based on the general surface tension of PDMS, which is around 20.4 mN/m. PDMS possesses the lowest surface tension with low viscosity, while PDMS possesses the highest surface tension in this range with high viscosity. However, the surface tension of some samples does not follow the viscosity value trend.

This study shows that PDMS synthesized via ROP has characteristics similar to hydrolysis-condensation. Previous studies have conducted comparative analyses of IR spectra of PDMS derived from both methods. The findings are presented in **Table 5**, where F-HC is the sample resulting from hydrolysis-condensation, and F-ROP is the sample resulting from ROP. However, the transmittance of the CH stretching vibration of the CH_3 groups in PDMS synthesized via the ROP method is more similar to that of commercial PDMS than that of samples produced through hydrolysis-condensation [20,31]. The FTIR analysis indicates that PDMS from the ROP method exhibits lower transmittance than the hydrolysis-condensation method. This suggests that PDMS synthesized by ROP tends to absorb more infrared (IR) energy. This difference is likely attributed to the denser and more homogeneous chemical structure of ROP-derived PDMS, which enhances interactions between the polymer molecules and IR radiation and increases absorption. This analysis is based on a visual comparison of spectrum patterns. Since quantitative transmittance data from IR spectra are not explicitly given in the reviewed articles.

Table 5 Functional group of commercial silicone oil and PDMS through ROP and hydrolysis-condensation [20,33].

Functional group	**Wavenumber (cm^{-1})**			
	Commercial low viscosity PDMS	**F-HC**	**F-ROP**	**Commercial high viscosity PDMS**
(1) Si-C stretching and CH_3 rocking	792.8 - 823.8;	784.0 - 862.2;	804;	815.1;
(2) Si-O-Si stretching	1,022.8; 1,111.9	1,007.9	1,084.4	1,099.1
(3) CH stretching of CH_3	2,905.5; 2,971.7	2,905.5; 2,961.7	2,905.4; 2,965.1	2,905.6; 2,969.6

Toxicity samples were tested using the Hen's Egg Test - Chorioallantoic Membrane (HET CAM). HET CAM is an *in vitro* testing method used to assess the potential irritation of a substance to the eye. This method utilizes the chorioallantoic membrane (CAM) in developing chicken embryos [51,52]. Based on HET CAM testing, PDMS samples from the ROP and hydrolysis-condensation processes were tested to be safe and did not contain toxic substances [2,17]. Although HET-CAM is reported to correlate 76 % with in vivo results (Draize test) [58], it doesn't always reliably predict human responses. The endpoints measured by HET-CAM - such as hemorrhage, coagulation, and vessel lysis - do not capture the full range of eye effects in humans. This method mainly assesses acute reactions and overlooks chronic effects or long-term toxicity. Additionally, the conditions of the chorioallantoic membrane do not fully mimic human eye conditions, as factors like pH, osmolarity, and tear film components are not well represented. As a result, *in vivo*, toxicity tests and further tests on long-term use are needed [59].

Explanation of the synthesis route and how the characteristics were obtained: According to the authors, the best route is the ROP route because of several significant advantages related to molecular control, as seen from the IR spectrum characterization, efficiency determined from the synthesis time, and product quality.

Conclusions

PDMS can be synthesized from ROP and hydrolysis-condensation processes. PDMS through ROP has a shorter process than hydrolysis-condensation. The relation between KOH concentration and the polymerization process in both processes has the same conclusion: KOH with a higher concentration is polymerized faster, underscoring the importance of catalyst concentration in both processes. Other parameters that must be considered in the ROP method are the purity of D4, the material ratio, and the polymerization time. In the hydrolysis-condensation method, other parameters that must be considered are the volume ratio of DCDMS:DCM, the reaction time and temperature during hydrolysis, and the sample characteristics from the hydrolysis process. Both methods also produced biocompatible samples for vitreous substitute applications according to the HET CAM test. However, although both methods produced PDMS suitable for vitreous substitution, ROP is more practical due to its efficient synthesis steps and reduced processing time. Ultimately, the choice between ROP and hydrolysis-condensation should be guided by the specific application requirements for PDMS. This comparative analysis reinforces the importance of selecting the appropriate synthesis method based on the desired product characteristics and consideration of synthesis efficiency PDMS as a vitreous substitute.

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