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NMR CHARACTERIZATION OF POLYMETHYLHYDROSILOXANE SYNTHESIZED USING DICHLOROMETHANE AND DIETHYL ETHER AS SOLVENT FOR VITREOUS SUBSTITUTE

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ABSTRACT

Polymethylhydrosiloxane (PMHS) was synthesized from dichloromethylsilane (DCHS) using the hydrolysis-condensation method with dichloromethane (DCM) or a diethyl ether (DE) as a solvent. We study the effect of solvent on the properties of the synthesized PMHS using ^{1}H-NMR and ^{13}C-NMR. It was found that both samples have three peaks (Si-H, Si-CH_3, and Si-CH_3) on ^{1}H-NMR measurement and one peak (Si-CH_3) on ^{13}C-NMR measurement. All of the peaks are characteristics of PMHS. There are no other elements related to the solvents, which indicated that the PMHS samples had been successfully synthesized with a high degree of purity. In addition, the possibility of structures formed in the PMHS samples was also obtained.

Keywords: Dichloromethane; Diethyl Ether; NMR; PMHS; Vitreous Humour

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INTRODUCTION

In the human eye, there is an important part called the vitreous humour. This fluid dominates by filling 80% of the human eye volume. This eye part is between the lens and the retina [1]. However, disturbances often occur in this vitreous humor, including retinal detachment [2-3]. Retinal detachment is a disorder of the vitreous humor caused by the retinal neurosensory layer being separated from its pigment epithelium. The leading factors are physical changes of the vitreous humor, a family history, a serious injury, and suffering from high myopia (about six diopters). It causes the retina to tear easily and become thinner [4].

Retinal detachment can be treated by replacing the vitreous humour with an artificial replacement fluid called a vitreous substitute [5-6]. The procedure is known as vitrectomy [7]. The recently developed material as a vitreous substitute is one type of an inorganic-organic hybrid polymer. This polymer consists of silicon-oxygen bond (Si-O) repeating units with a hydrogen atom and methyl group as the main substituents of the silicon atom, which is known as polymethylhydrosiloxane (PMHS) [8]. The advantages of PMHS are non-toxic,

transparent, stable, and colorless [9-10]. PMHS can be obtained by synthesizing dichloromethylsilane (DCHS) through the hydrolysis-condensation method [8,11]. This precursor is easier to obtain and has a lower price than the precursor of octamethylcyclotetrasiloxane (D4) that is commonly used to produce commercial polydimethylsiloxane (PDMS) in Indonesia.

In order to use the DCHS as a monomer, the chlorine in the molecule should be removed and replaced with a hydroxyl (OH) as functional group. The OH functional group will be reacted in the condensation polymerization process and formed PMHS [12].

A previous study has reported the synthesis of PMHS with low viscosity using dichloromethane (DCM) as a solvent. The confirmation of success was based on the main functional group PMHS obtained using Fourier Transform Infra-Red (FTIR) spectroscopy [12]. Therefore, further characterization is needed to ensure that the synthesized sample has the characteristics of PMHS. One of the important methods for characterizing materials and studying polymer chemistry is nuclear magnetic resonance (NMR) spectroscopy [13]. ^{1}H-NMR and ^{13}C-NMR are NMR spectroscopy commonly used for compound analysis [14]. In this research, we used ^{1}H-NMR and ^{13}C-NMR to characterize PMHS samples as the substitute for vitreous humor in the human eye that were synthesized from DCHS using different solvents, namely DCM and diethyl ether (DE) solvents.

METHOD

Hydrolysis-Condensation

The synthesis process in detail can be seen in the previous research [12]. The PMHS synthesis was carried out using variations of solvents, namely DCM and DE. Firstly, the DCHS was dissolved using solvent with a ratio of 1:1. Then the solution was mixed with water as described previously to form hydroxyl functional group [12]. Equation 1 shows the chemical reaction of the hydrolysis process of PMHS.

$$CH_3SIHCl_2 + 2H_2O \rightarrow CH_3SiH(OH)_2 + 2HCl \quad (1)$$

The condensation process was carried out for 24 hours using DCM solvent and 2 hours for the DE solvent sample. Then, the samples were purified and evaporated to obtain the PMHS, as described in the previous research [15]. The samples synthesized using DCM are represented by code A, while DE is represented by code B.

NMR Characterization

NMR characterization was carried out to determine the characteristics and content of PMHS, such as functional groups that can be identified from the chemical shift of the sample. The preparation for the NMR measurement was carried out by dissolving a small amount of the samples in deuterated chloroform ($CHCl_3$). NMR measurements were carried out using ^{1}H-NMR and ^{13}C-NMR 500 MHz Agilent-VNMRS500 at The Physical and Chemical Research Institute (RIKEN), Japan.

RESULTS AND DISCUSSION

PMHS with a low viscosity of 1.10 Pa.s was obtained using DCM solvent. Meanwhile, the medium viscosity of 2.10 Pa.s was obtained using DE solvent. Both of these viscosities have met the viscosity standard as a vitreous substitute.

Figure 1 and Figure 2 show the NMR characterization results of the sample using DCM solvent (sample A). There are three peaks in the ^{1}H-NMR characterization results as shown in Figure 1. The first peak at 0.070 ppm is the first peak of the H atom on the first Si-CH_3. The second peak at 0.201-0.203 ppm is the H atom on the second Si-CH_3. The third peak at 4.710-4.715 ppm is the H atom on Si-H. The ^{13}C-NMR characterization result of sample A can be seen in Figure 2. One peak is found at 0.853 ppm which is the peak of the C atom in Si-CH_3.

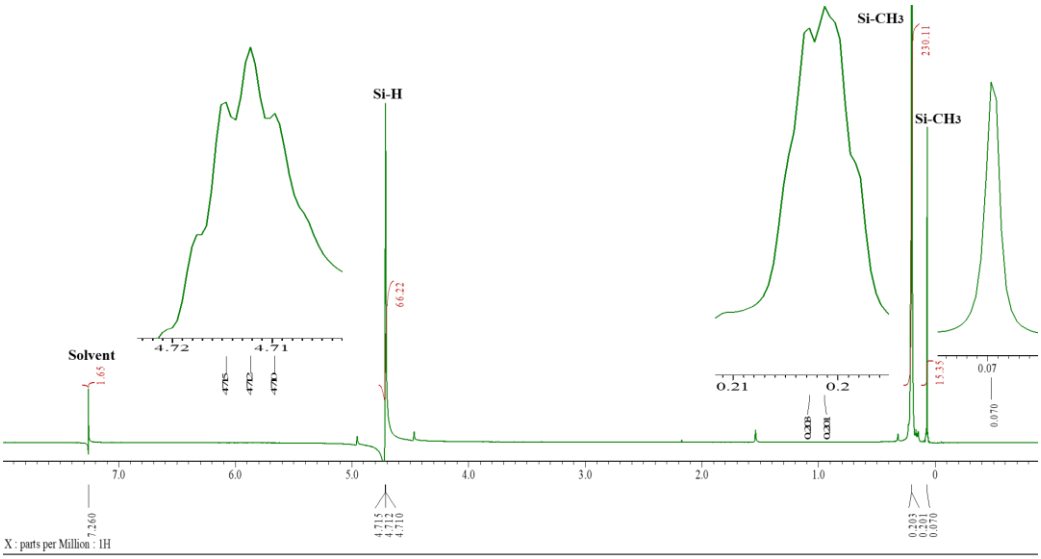

Figure 1. ^{1}H-NMR characterization of sample A.

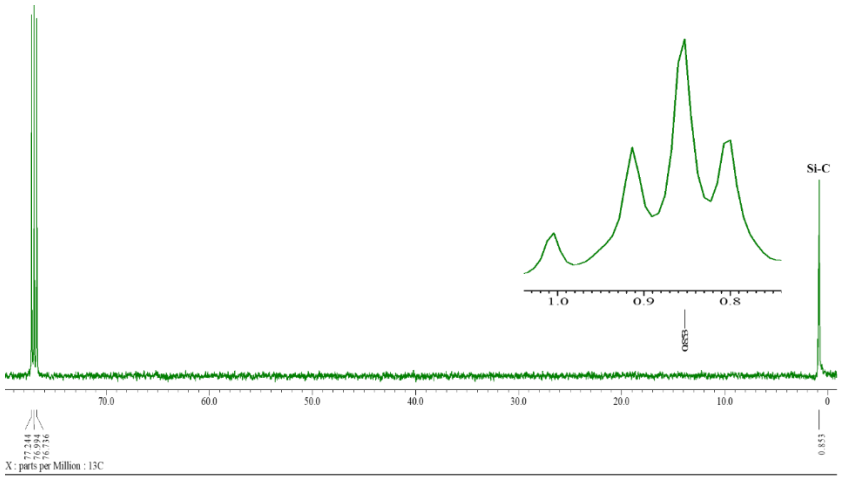

Figure 2. ^{13}C-NMR characterization of sample A.

The ^{1}H-NMR characterization of the sample using DE solvent (sample B) is shown in Figure 3. There are three peaks in the ^{1}H-NMR characterization results. It is appropriate with PMHS which has a three H environment like in the PMHS structure in Figure 5. The first peak at 0.069 ppm is the first peak of the H atom on Si-CH_3. The second peak at 0.199-

0.202 ppm is the H atom on the first Si-CH_3. The third peak at 4.711-4.714 ppm is the H atom on Si-H. The ^{13}C-NMR characterization showing the C atom in Si-C for sample B can be seen in Figure 4. The ^{13}C-NMR characterization results showed one peak at 0.857 ppm which is the peak of the C atom in Si-CH_3.

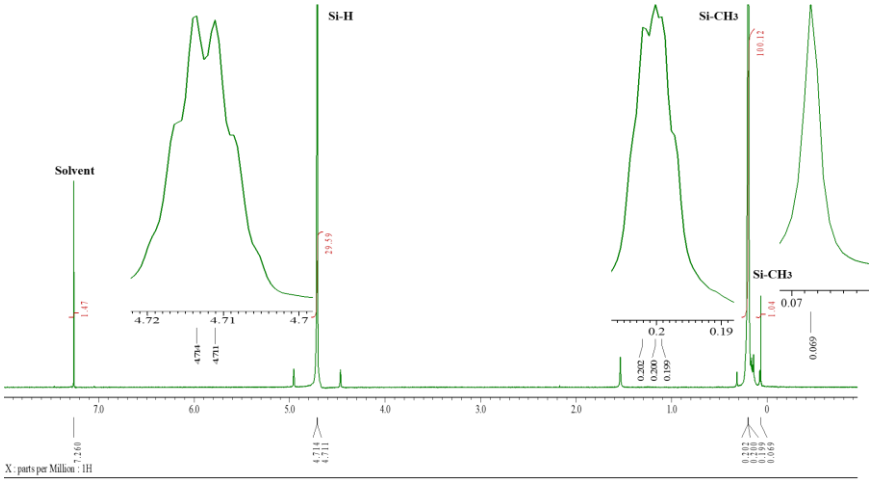

Figure 3. ^{1}H-NMR characterization of sample B

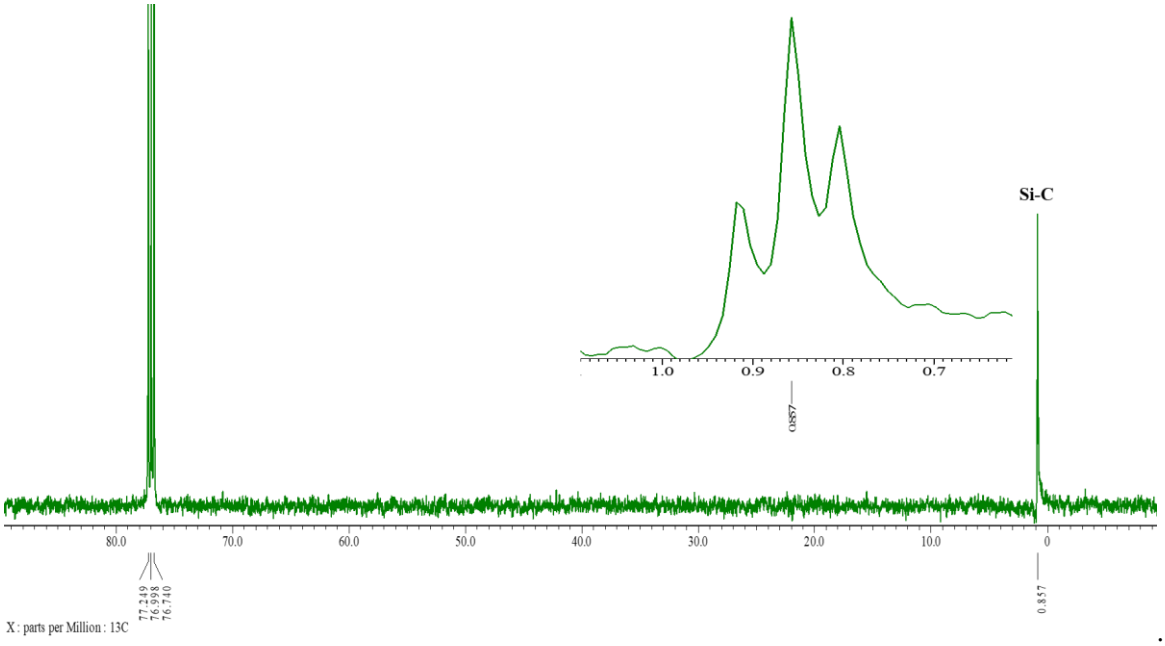

Figure 4. ^{13}C-NMR characterization of sample B

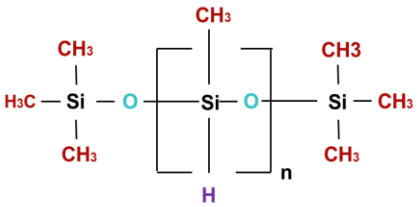

Figure 5. PMHS chemical structure.

Table 1. ^{1}H-NMR characterization results on samples A and B.

Functional Group	δ(ppm)	
	A	B
Si-CH_3	0.070	0.069
Si-H	4.710-4.715	4.711-4.714
Si-CH_3	0.201-0.203	0.199-0.202

Table 2. ^{13}C-NMR characterization results on samples A and B.

Functional Group	δ (ppm)	
	A	B
Si-CH_3	0.853	0.857

NMR characterization results in Table 1 and Table 2 show that both samples A and B have a typical peak for PMHS. There is no difference in the characterization results of the two NMR (^{1}H-NMR and ^{13}C-NMR) for samples using DE and DCM solvents. No impurities were found in PMHS samples either from both solvents. These results show that the synthesized PMHS is perfectly formed with both solvents. NMR results strengthen the FTIR information from previous studies [12]. Both samples had the same number of peaks which is a typical characteristic of PMHS with slight chemical shifts. From NMR results, the possible PMHS structures obtained from both samples are$-O-Si(Me)-\{-OSiH(Me)-OSiH(Me)\}n-O-SiHMe-$

However, for complete information about the structure and form of bonds, it is necessary to measure the PMHS samples using ^{29}Si-NMR.

CONCLUSION

^{1}H-NMR and ^{13}C-NMR characterization of PMHS samples has been carried out with the aim of knowing their structure and chemical content. The NMR characterization results showed that both samples had typical PMHS characteristics, namely H atoms in Si-H and H atoms in Si-CH_3 with a slight chemical shift. There was no significant difference in the NMR characterization results for both ^{1}H-NMR and ^{13}C-NMR for samples using DE and DCM solvents. In addition, no impurities from DCM or DE solvents were found in the samples. These results show that the synthesized PMHS samples formed perfectly with these two solvents. The possible structures formed in the synthesized samples were also obtained. However, ^{29}Si-NMR needs to be carried out for further study to obtain complete information about the structure and form of the bonds of the PMHS samples.

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