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Partial or Total Silylation of Polytetramethylene Glycol with Trimethylchlorosilane

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The silylation reaction of polytetramethylene glycol (PTMG) with trimethylchlorosilane (TMS) in DMSO was studied as the first step of the synthesis of new fluorinated polyether glycol. The extent of silylation was measured by ¹H-NMR, and the silylation product was characterized with FTIR, ¹H-NMR. The effects of the experimental conditions, i.e., reaction time and temperature, silylation reagent concentration (TMS/OH molar ratio) were investigated. The increase in reaction temperature and reaction time favored the silylation yields. After grafting reaction and ultimate deprotection of the silylated PTMG, novel fluorinated polyether glycol could be readily recovered.

Keywords: modification; silylation; silylation yield; fluorinated polyether glycol

1 Introduction

Polytetramethylene glycol (PTMG) is linear aliphatic polyether of growing technical importance. This fact is caused by the application of PTMG as a component of thermoplastic polyurethanes. In this field, PTMG has replaced the classic polyesterdiols due to its good hydrolytic stability. Furthermore, PTMG is used as soft components in elastomers such as thermoplastic polyetheresters, thermoplastic polyetheramides, polyurethane fibers and crosslinked polyurethane elastomers (1–5).

To improve the properties and extend the possibilities of the application of polytetramethylene glycol, the chemical modification of the PTMG structure is very important. In some publications, the modifications of PTMG have been described (6–8). The author has also discussed the modification of PTMG by grafting hexafluoropropylene (HFP) onto the PTMG main chain (9). However, it was found that a small part of the terminated hydroxyl groups of PTMG had been reacted with HFP. This will affect the use of PTMG as chemical intermediates. Therefore, it is necessary that the hydroxyl groups of PTMG be protected. Protection of hydroxyl groups with the trimethylsilyl group is performed

on a daily basis in research laboratories throughout the world. This has been reported in many literatures. For example, Wang investigated biodegradable brush-like graft polymerization with hydroxypropyl cellulose as the backbone by the silylation method (10) and Nouvel discussed the silylation of dextran with hexamethyldisilazane (11).

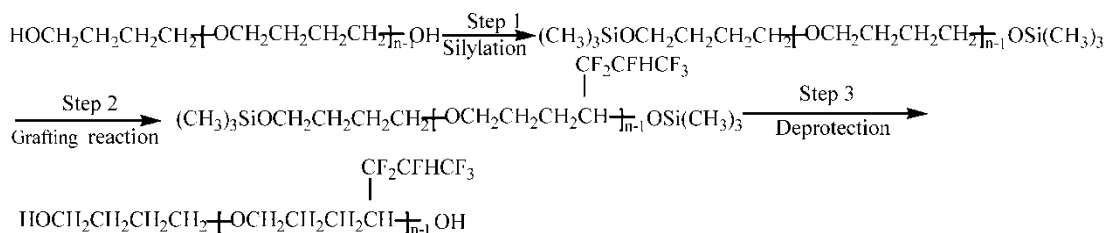
This paper mainly reports the partial or total silylation of PTMG using trimethylchlorosilane (TMS) in depth for the first time at least to the best of our knowledge. Influence of various factors on the silylation yield (i.e., the degree of protection) was investigated. Factors, such as reaction temperature, reaction time and silylation reagent concentration (TMS/OH ratio), were studied. The second part of this paper will report grafting HFP onto silylated PTMG and the deprotection of grafting product. The entire reaction strategy is given in Scheme 1.

2 Experimental

2.1 Materials

Polytetramethylene glycol ($M_n = 1000$) were purchased from Mitsubishi Chemical and dried under a reduced pressure at 100°C for 8 h. Trimethylchlorosilane (TMS), dimethyl sulfide (DMSO), triethylamine (Et₃N), anhydrous sodium sulfate, methanol, potassium carbonate and di-*tert*-butyl peroxide (DTBP) were purchased from China Medicine, Shanghai Chemical Reagent Corporation. Hexafluoropropylene was used as received from Zhejiang Juhua Co. Ltd. DMSO was refluxed over CaH₂. Materials, other than the

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Sch. 1. Synthesis of fluorinated polyether glycol.

above mentioned were used without further purification unless otherwise specified.

2.2 PTMG Silylation

A typical procedure was as follows. A quantity of PTMG (130 g) was dissolved in DMSO (150 ml) in a previously dried and nitrogen purged four-necked round bottom flask. The mixture was stirred until completely dissolved, the desired amount of TMS and triethylamine were added under nitrogen flow with a previously dried syringe. The reaction medium was kept at the desired temperature in a suitable time. After cooling to room temperature slowly, the mixture was then filtered and purified by distillation under reduced pressure.

2.3 Grafting HFP onto Silylated PTMG

A 500 ml Hastelloy lined autoclave equipped with a “flip-flop” stirrer, pressure gauge, bursting disc (maximum working pressure approx. 20MPa) and inlet/outlet valve was charged with 150 g molten silylated PTMG and 0.0164 mol di-*tert*-butyl peroxide. The reaction vessel was closed, frozen in an acetone/liquid nitrogen mixture and placed under vacuum for several minutes. Then the required amount of HFP (400 g) was introduced. After being heated to 140°C with stirring for 6 h in a thermostatically controlled furnace, the autoclave was cooled to room temperature. The product was collected and purified by distillation under reduced pressure.

2.4 Deprotection of the Grafted Silylated PTMG

The silylated graft product was dissolved in a slight excess of methanol with respect to the number of $\text{---O---Si(CH}_3\text{)}_3$ group and a small amount of potassium carbonate was then added. After 2 h at room temperature, the mixture was washed to neutrality with water. Then the mixture was dried over anhydrous sodium sulfate in 36 h, and the sodium sulfate was filtered off. The deprotected product was further dried under vacuum.

2.5 Measurements

$^1\text{H-NMR}$ spectra were respectively recorded on a Bruker AC 300 NMR spectrometer with tetramethylsilane (TMS) as the internal standard and deuterated chloroform (CDCl_3) as

solvent unless otherwise stated. For the $^1\text{H-NMR}$ experiment, the hydrogen atom in CDCl_3 was taken as 7.24 ppm and all other peaks were assigned with respect to it. Infrared analysis was carried out on a Bruker Equinox 55 FTIR spectrometer and the spectra were recorded in the range of 4000 to 500 cm^{-1} .

3 Results and Discussion

3.1 Silylation Reaction of PTMG

As the first step in Scheme 1, the silylation reaction was chosen because it presents many prominent advantages:

- Fast and easy hydroxyl protection.
- Stability of resulting silylether under neutral conditions. This will not affect subsequent grafting reaction.
- Easy deprotection of ---Si(Me)_3 by acid or basic hydrolysis. The deprotection step can be achieved in a short time.

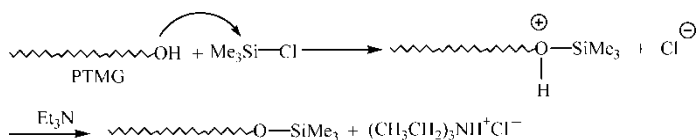
The silylation mechanism with TMS is shown in Scheme 2. The hydroxyl function groups react with TMS, to give silylated PTMG and HCl, which then reacts with Et_3N yielding $(\text{CH}_3\text{CH}_2)_3\text{NH}^+\text{Cl}^-$ as a product. Et_3N is used to neutralize the generated HCl in order to make silylation reaction proceed in the advantageous way.

3.2 Silylation Yields

Silylation yields were calculated by $^1\text{H-NMR}$ in CDCl_3 depending on the extent of silylation. Silylation yields (y) were calculated using Equation (1):

$$y = \frac{A_{\text{OSiMe}_3}}{A_{\text{methyleneH}}} \times 300 \quad (1)$$

where A_{OSiMe_3} and $A_{\text{methyleneH}}$ are the respective areas of the ---OSiMe_3 group (at 2.03 ppm in CDCl_3), and of the methylene (not adjacent to oxygen) protons centered at 1.68 ppm in CDCl_3 (Figure 1). Similar silylation yields were obtained



Sch. 2. Silylation mechanism with TMS using Et_3N .

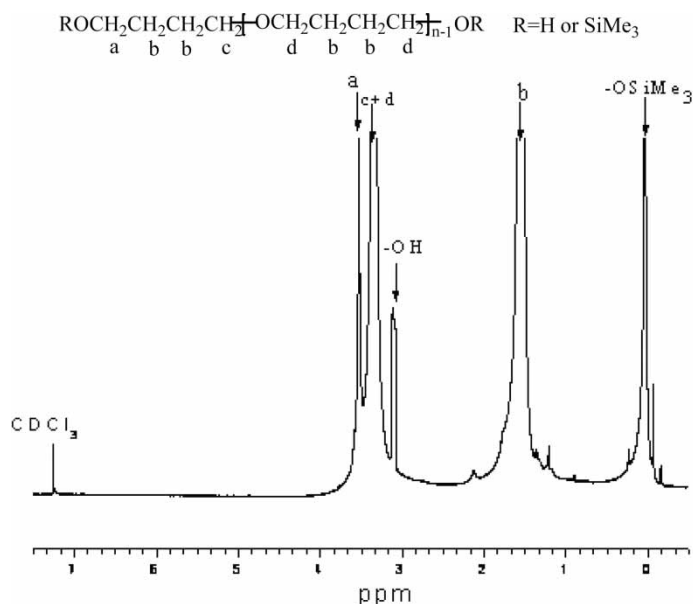


Fig. 1. $^1\text{H-NMR}$ spectrum of partially silylated PTMG in CDCl_3 .

using Equation (1). From the silylation yield, one can readily determine the degree of substitution (DS), i.e., the number of protected hydroxyl functions per PTMG unit. DS was calculated from the silylation yield using Equation (2):

$$\text{DS} = \frac{2y}{100} \quad (2)$$

3.3 Influence of Reaction Time and Temperature

The reaction temperature and time play a significant role on the effect of silylation of PTMG. As to be expected, the silylation yield increased with the increment of reaction temperature and time. It can be seen from Figure 2 that an increase of reaction temperature from 30 to 80°C resulted in an increment of the silylation yield. The reason for this significant increase of silylation yield by raising temperature was probably due to the favorable effect of temperature on compatibility of the reaction ingredients (12). In addition, the hydroxyl groups of PTMG form extensive hydrogen bonding networks within the matrix, and the reaction of TMS with hydroxyl group requires the breaking of hydrogen bond (13). During the silylation process, increasing temperature favored breaking such hydrogen bonds, diffusing the silylation agent, thus enhanced the reaction rate. The fastest silylation reaction and the highest silylation yield (97%) were obtained at 80°C.

Figure 2 also shows the effect of reaction duration on the silylation yield of the silylated PTMG. Clearly, the silylation yield increased with the increment of reaction time. This increment of silylation, by prolonging the duration of reaction, was a direct consequence of the favorable effect of time on diffusion of the reactants between TMS and PTMG molecules.

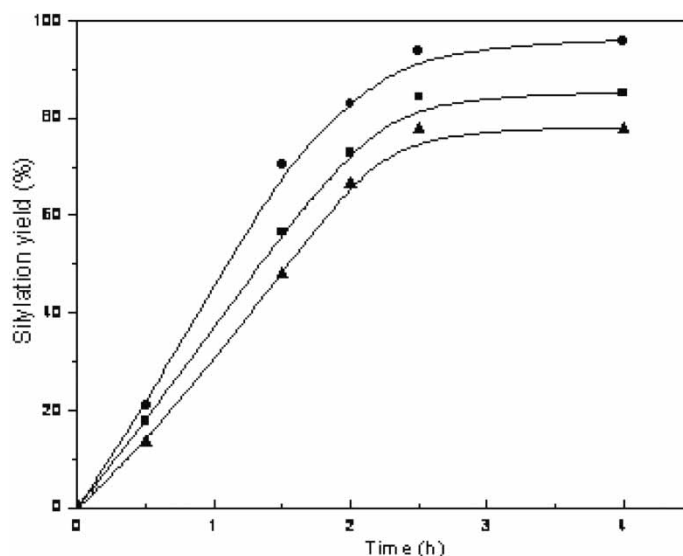


Fig. 2. Change in silylation yield with reaction time at different temperatures (\blacktriangle 30°C; \blacksquare 50°C; \bullet 80°C) with 1.05 mol TMS per mol OH. Silylation yields were calculated from Equation (1).

3.4 Influence of Silylation Reagent Concentration

The effect of TMS concentration on the silylation yields was investigated and the results are shown in Table 1. An increase in TMS/OH molar ratio enhanced the yield of silylation. The reason may be that the increment of TMS concentration signifies the increase in the number of silylation reagent in the solution. Therefore, this increases the chance of hydroxyl in PTMG encountering more TMS units. When the TMS/OH ratio is 1.25, total silylation of PTMG was achieved at 80°C for 4 h. This can be further proven by IR spectroscopy, which displays the complete disappearance of the hydroxyl absorption band at 3467 cm^{-1} (Figure 3).

3.5 IR Analysis

A comparison of the FTIR spectra of PTMG to that of totally silylated PTMG (TMSPTMG) is shown in Figure 3. As illustrated in the spectrum of TMSPTMG, except that the original

Table 1. Dependence of silylation yield and DS on TMS/OH molar ratio. Each silylation was carried out in DMSO at 80°C for 4 h

TMS/OH molar ratio	Silylation yield (%) ^a	DS ^b
0.25	51	1.0
0.50	69	1.4
0.75	81	1.6
1.05	97	1.9
1.25	100	2.0

^aCalculated from Equation 1.

^bCalculated from Equation 2.

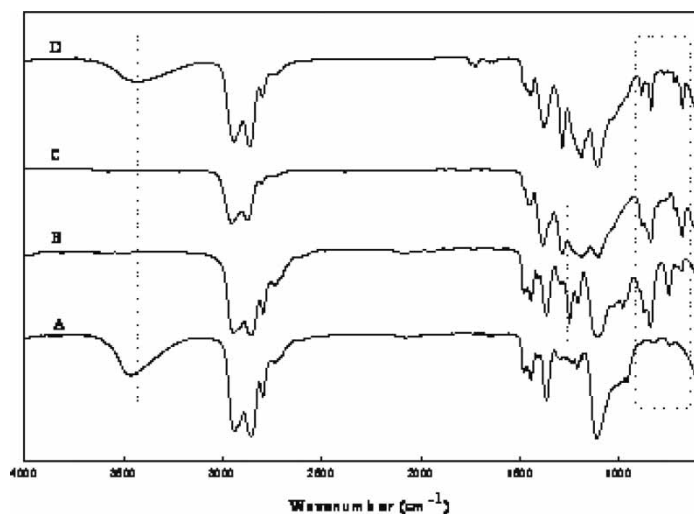


Fig. 3. IR spectra of PTMG (A), TMSPTMG (B), TMSPTMG-g-HFP (C), PTMG-g-HFP.

CH₂ and COC characteristic peaks of PTMG remain, six new peaks corresponding to the Si-O and Si-C (14, 15) are observed: the characteristic absorption bands of Si-CH₃ at 1250, 874, 840 and 750 cm⁻¹; the absorption bands corresponding to Si-O at 1150 cm⁻¹ and 986 cm⁻¹. At the same time, the hydroxyl stretching band at 3467 cm⁻¹ are not observed in the FTIR spectrum of TMSPTMG, which indicated the hydroxyl band been completely substituted. Figure 3 also shows the grafted TMSPTMG (TMSPTMG-g-HFP) spectrum. In the TMSPTMG-g-HFP spectrum, there are new absorption bands dealing with the vibration absorption of C-F bond at 1190 cm⁻¹, 1287 cm⁻¹ and 680 cm⁻¹, indicating that the reaction of grafting HFP onto TMSPTMG had occurred (9). The trimethylsilyl groups of obtained TMSPTMG-g-HFP were completely unprotected by reaction in a methanol/K₂CO₃ mixture. As shown in the spectrum of unprotected TMSPTMG-g-HFP (PTMG-g-HFP) of Figure 3, the disappearance of all characteristic peaks for the Si-Me group and the recurrence of the hydroxyl characteristic peaks mean that the trimethylsilyl groups were successfully cleaved.

3.6 ¹H-NMR spectra

Figure 4 displays the ¹H-NMR spectra of PTMG (A) and totally silylated PTMG (B). In the spectrum of PTMG, the signal at 3.08 ppm is assigned to the hydroxyl protons (-CH₂O^H) and the signal at 3.60 ppm is specific for the methylene protons (-C^H₂OH). Moreover, the signals at 3.43 ppm dealing with -OC^H₂CH₂CH₂C^H₂O- protons and the peaks at 1.62 ppm corresponding to the -CH₂C^H₂C^H₂CH₂O- protons are also observed. Compared with the spectrum of PTMG, a new signal at 0.10 ppm, corresponding to the OSi(C^H₃)₃ protons, is observed in spectrum of silylated PTMG, and furthermore, the signal corresponding to hydroxyl protons totally disappeared.

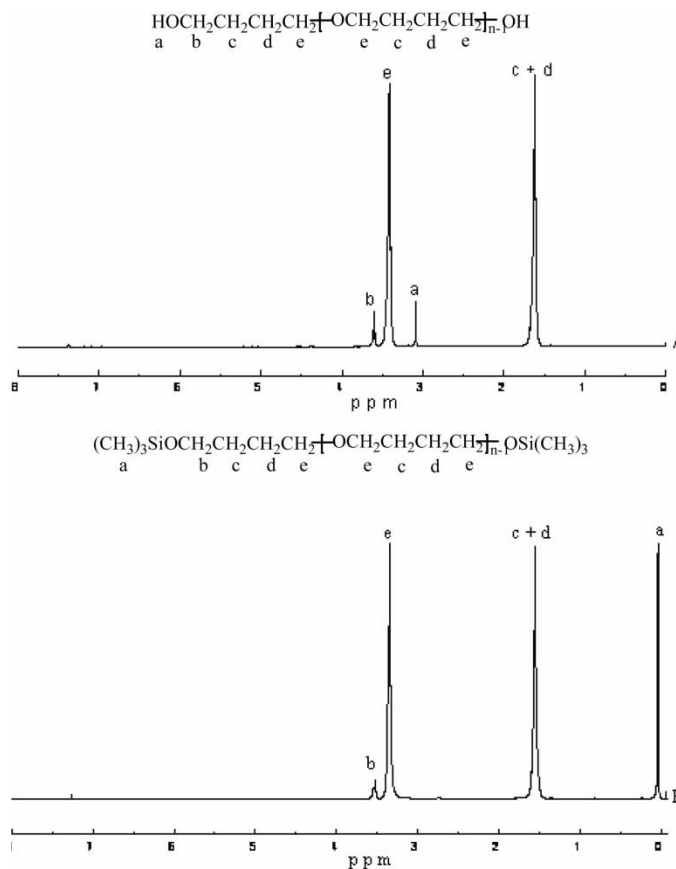


Fig. 4. ¹H-NMR spectra of PTMG (A) and totally silylated PTMG (B).

4 Conclusions

The silylation reaction of PTMG, by means of TMS, was carried out in DMSO. The influence of various parameters on the extent of silylation was studied. It was found that silylation yield increased with the increment of reaction time, reaction temperature and TMS/OH molar ratio. Totally silylated PTMG was obtained at 80°C for 4 h with TMS/OH ratio equal to 1.25. The reaction of silylated PTMG grafting HFP and the unprotection of grafting product could be readily realized.

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