Acetylation Reaction of Polytetramethylene Glycol with Acetic Anhydride in Pyridine

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ABSTRACT: The acetylation reaction of polytetramethylene glycol (PTMG) with acetic anhydride in pyridine was studied. The extent of acetylation was measured by ^{1}H-NMR, and the acetylation product was characterized with FTIR, ^{1}H-NMR, and ^{13}C-NMR. The effects of the experimental conditions, i.e., reaction time and temperature, acetylation reagent concentration (anhydride and hydroxyl molar ratio), were investigated. The increase in reaction temperature and reaction time favored the acetylation yields. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1138–1142, 2007

Key words: modification; acetylation; NMR; acetylation yield; FTIR

INTRODUCTION

Polytetramethylene glycol (PTMG) is a liner aliphatic polyether of growing technical importance because of its application as component of thermoplastic polyurethanes. In this field, PTMG has replaced the classic polyesterdiols because of 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 application of polytetramethylene glycol, 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 PTMG main chain.[9] But 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 acetic anhydride (Ac_2O) is performed on a daily basis in research laboratories throughout the world. This has been reported in the literature. For example, Fang discussed acetylation of wheat-straw hemicellulose in a new nonaqueous swelling system[10] and Sun investigated the acetylation of sugarcane bagasse using *N*-bromosuccinimide (NBS) as a catalyst.[11] Acetylation of wood using acetic anhydride has been well studied by Rowell to improve dimensional stability and biological resistance of wood for many years.[12] Acetylation of wood has already been used on a commercial basis in Japan.

To the best of our knowledge, this paper is the first to report in depth the acetylation of PTMG using acetic anhydride. Influence of various factors on the acetylation yield (i.e., the degree of protection) was investigated. Factors such as reaction temperature, reaction time, and acetylation reagent concentration (Ac_2O/OH ratio) were studied. The second part of this paper will report grafting HFP onto acetylated PTMG and the deprotection of grafting product. The whole reaction strategy was given in Scheme 1.

EXPERIMENTAL

Materials

Polytetramethylene glycol ($M_n = 1000$) were purchased from Mitsubishi Chemical and dried under a reduced pressure at 100°C for 8 h. Pyridine, acetic anhydride, acetone, methanol, ethanol, chloroform, HCl, potassium carbonate, and di-*tert*-butyl peroxide (DTBP) were purchased from China Medicine, Shanghai Chemical Reagent Corp. Hexafluoropropylene was used as received

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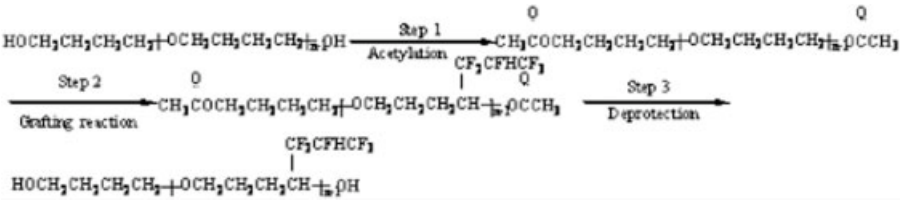

Scheme 1 Synthesis of fluorinated polyether glycol.

from Zhejiang Juhua Co. All these materials were used without further purification unless otherwise specified.

Acetylation of PTMG

A typical procedure was as follows. A quantity of PTMG (200 g) was dissolved in pyridine (100 mL) in a 500 mL round bottom three-necked flask. The mixture was stirred until completely dissolved and then 50 g acetic anhydride was slowly dropped into this solution. The reaction mixture was stirred for 4 h at 90°C. After cooling slowly, the mixture was then thoroughly washed with ethanol and acetone to remove the unreacted acetic anhydride and acetic acid by-product. The products were then dried at 60°C for 16 h under vacuum.

Acetylation yields

Acetylation yields were calculated by ^{1}H-NMR in $CDCl_3$ depending on the extent of acetylation. Acetylation ratios were calculated using eq. (1):

$$\text{yield } (\%) = \frac{A_{\text{OCOMe}}\ (\%)}{A_{\text{methylene H}}} \times \frac{100}{9.1} \tag{1}$$

where A_{OCOMe} and $A_{\text{methylene H}}$ are the respective areas of the —$OCOCH_3$ group (at 2.03 ppm in $CDCl_3$), and of the methylene (not adjacent to oxygen) protons centered at 1.68 ppm in $CDCl_3$ (Fig. 1). Similar acetylation yields were obtained using eq. (1). From acetylation yield, one can readily determine the degree of substitution (DS), i.e., the number of protected hydroxyl functions of per PTMG unit. DS was calculated from the acetylation yield using eq. (2):

$$\text{DS} = \frac{2\ \text{yield } (\%)}{100} \tag{2}$$

Grafting reaction and deprotection

A 500 mL Hastelloy lined autoclave equipped with a ''flip-flop'' stirrer, pressure gauge, bursting disc (maximum working pressure approx. 20 MPa), and inlet/outlet valve was charged with 150 g molten acetylated 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 150°C with stirring for 8 h in a thermostatically controlled furnace, the autoclave was cooled to room temperature. The product was collected and purified by distillation under reduced pressure. Then the acetylated graft product was dissolved in acetone and methanol mixture and a slight excess of potassium carbonate aqueous solution with respect to the num-

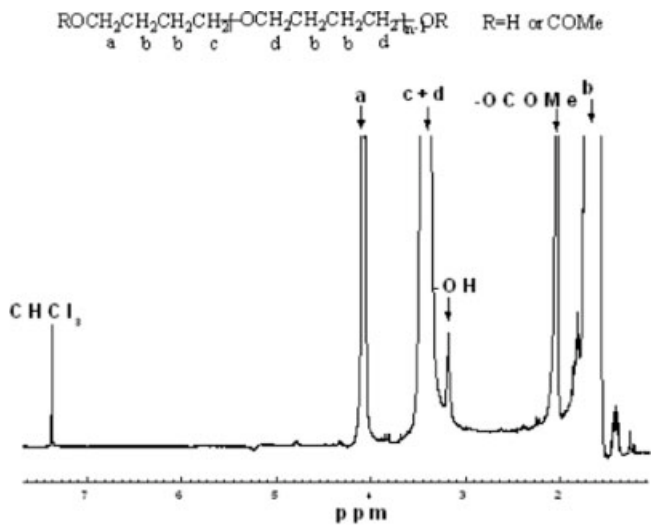

Figure 1 ^{1}H-NMR spectrum of (partially) acetylated PTMG in $CDCl_3$.

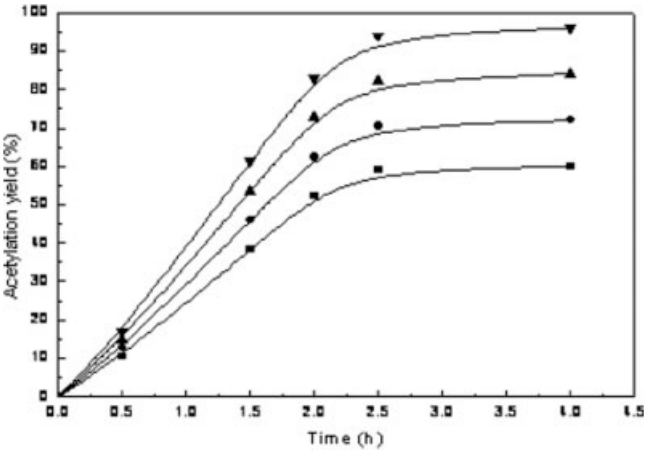

Figure 2 Change in acetylation yield (%) with reaction time at different temperatures (■ – 80°C; ● – 90°C; ▲ – 100°C; ▼ – 115°C) with 3 mol Ac_2O per mol OH. Acetylation yields were calculated from eq. (1).

ber of —O—(C=O)—CH_3 group was then added. After 5 h at 50°C, the pH of the product was adjusted to 3 by dropwise addition of 15% HCl. The solvent, acetic acid, and water were evaporated under high vacuum (10 mmHg) at 50°C. The crude product was again dissolved in acetone and the precipitated KCl salt was filtered off. Viscous oil was obtained by distilling off acetone. It was washed twice with chloroform. The deprotected product was further dried under vacuum.

Measurements

^{1}H-NMR and ^{13}C-NMR spectra were respectively, recorded on a Bruker AC 300 NMR spectrometer and on a Bruker AC 400 NMR spectrometer with tetramethylsilane (TMS) as internal standard and deuterated chloroform ($CDCl_3$) as solvent unless otherwise stated. For ^{1}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 4000–500 cm^{-1}.

TABLE I
Dependence of Acetylation Yield and DS on Ac_2O/OH Molar Ratio

Ac_2O/OH molar ratio	Acetylation yield[a] (%)	DS[b]
1.5	58	1.2
2	71	1.4
2.5	89	1.8
3	96	1.9
4	100	2.0

Each acetylation was carried out in pyridine at 115°C for 4 h.
[a] Calculated from eq. (1).
[b] Calculated from eq. (2).

RESULTS AND DISCUSSION

Influence of reaction time and temperature

The reaction temperature and time play a significant role on the effect of acetylation of PTMG. As to be expected, the acetylation yield increased with the increment of reaction temperature and time. It can be seen from Figure 2 that an increase of reaction temperature from 80 to 115°C resulted in an increment of the acetylation. The reason for this significant increase of acetylation by raising temperature was probably due to the favorable effect of temperature on compatibility of the reaction ingredients.[13] In addition, the hydroxyl groups of PTMG form extensive hydrogen bonding networks within the matrix, and the reaction of the anhydride with hydroxyl group requires the breaking of an hydrogen bond.[14] During the acetylation process, increasing temperature favored breaking such hydrogen bonds, diffusing the esterifying agent, thus enhanced the reaction rate. The fastest acetylation reaction and the highest acetylation yield (96%) were obtained at 115°C.

Figure 2 also shows the effect of reaction duration on the acetylation yield of the acetylated PTMG. Clearly, the acetylation yield increased with the increment of reaction time. This increment of acetylation by prolonging the duration of reaction was direct consequence of the favorable effect of time on diffusion of the reactants between the acetic anhydride and PTMG molecules.

Influence of acetylation reagent concentration

The effect of acetic anhydride concentration on the acetylation yields was investigated and the results

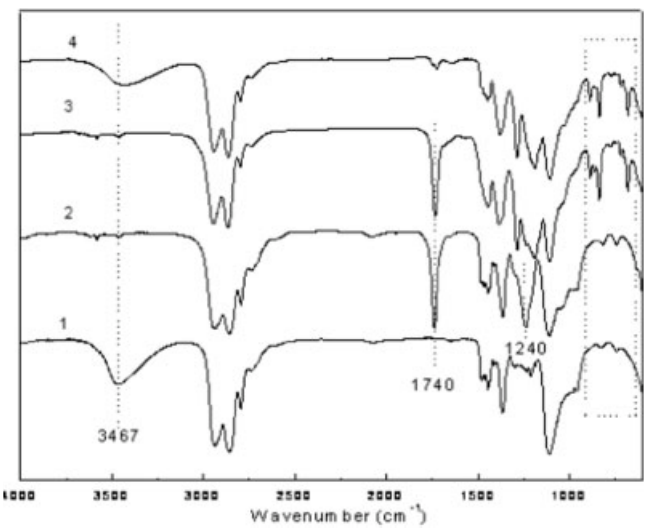

Figure 3 IR spectra of unmodified PTMG (spectrum 1), acetylated PTMG (spectrum 2), acetylated PTMG grafting HFP product (spectrum 3), and AC_2O-deprotected PTMG graft product (spectrum 4).

are shown in Table I. An increase in Ac_2O/OH molar ratio enhanced the yield of acetylation. The reason may be that the increment of the acetic anhydride concentration means the increase in the number of acetylation reagent in the solution. Therefore, this increases the chance of hydroxyl in PTMG encountering more anhydride units. When Ac_2O/OH ratio is 4, complete acetylation of PTMG was achieved at 115°C for 4 h. This can be further evidenced by IR spectroscopy shown in Fig. 3, which displays the complete disappearance of the hydroxyl absorption band at 3467 cm^{-1}.

FTIR spectra

To determine whether a chemical reaction between PTMG and acetic anhydride was taking place, samples were subjected to analysis by FTIR spectroscopy. Figure 3 shows FTIR spectra of unmodified PTMG (spectrum 1) and acetylated PTMG (spectrum 2). As illustrated in Figure 2, three major changes are observed in the FTIR spectrum of acetylated PTMG (spectrum 2) when compared with that of PTMG (spectrum 1): (1) a disappearance in the hydroxyl stretching band at 3467 cm^{-1}; (2) an increase in the carbonyl stretching absorbance at

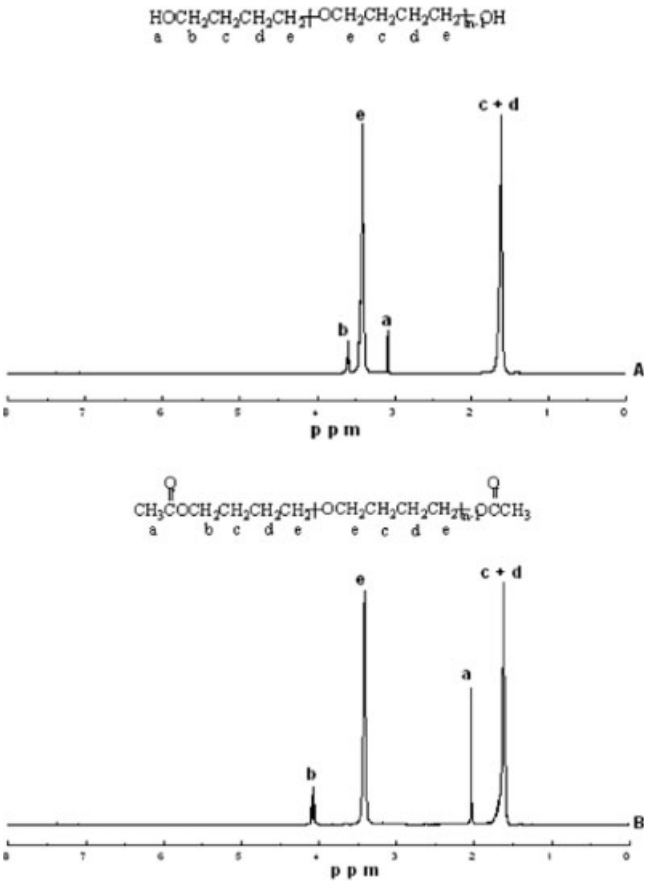

Figure 4 ^{1}H-NMR spectra of PTMG (A) and acetylated PTMG (B).

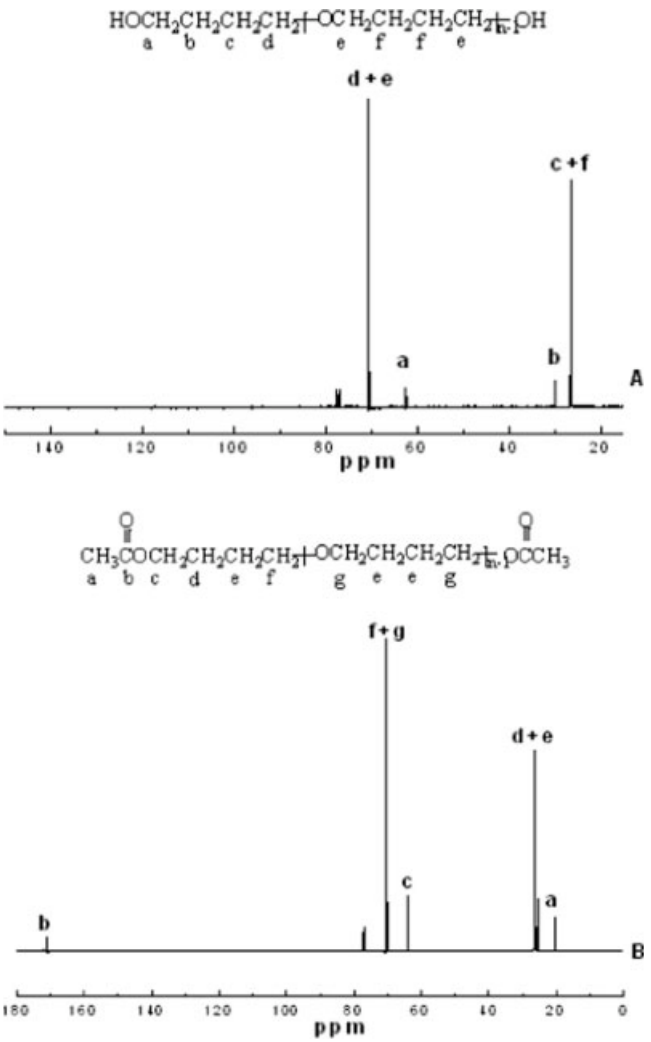

Figure 5 ^{13}C-NMR spectra of PTMG (A) and acetylated PTMG (B).

1740 cm^{-1}; (3) an enhancement in carbon–oxygen (C—O) stretching at 1240 cm^{-1} in an —O—(C=O)—CH_3 group. The absorbance at 2939, 2856, 2796, 1467, 1447, 1368, and 1112 cm^{-1} seen in spectrum 1 are associated with native PTMG. The disappearance of peaks in region 1840–1760 cm^{-1} and at 1700 cm^{-1} in spectrum 2 indicated that the product is free of the unreacted acetic anhydride and the by-product, acetic acid.[11] Figure 3 also shows the spectrum of acetylated PTMG grafting HFP product (spectrum 3). In the spectrum 3, there are new absorption bands dealing with the vibration absorption of C—F bond at 1190, 1287, and 680 cm^{-1}, indicating that the reaction of grafting HFP onto acetylated PTMG had been occurred.[9] The acetyl groups of obtained acetylated PTMG grafting product were completely deprotected by reaction in 15% HCl. As shown in the spectrum of AC_2O-deprotected PTMG graft product of Figure 3, the disappearance of all the characteristic peaks for the —O—(C=O)—CH_3 group

and the recurrence of the hydroxyl characteristic peaks mean that the acetyl groups were successfully cleaved.

^{1}H and ^{13}C-NMR spectra

Figure 4 displays the ^{1}H-NMR spectra of PTMG (A) and acetylated PTMG (B). In the spectrum of PTMG, the signal at 3.08 ppm is assigned to the hydroxyl protons (—$CH_2O\mathbf{H}$) and the signal at 3.60 ppm is specific for the methylene protons (—$C\mathbf{H}_2OH$). Besides, the signals at 3.43 ppm dealing with —$OC\mathbf{H}_2$-$CH_2CH_2C\mathbf{H}_2O$— protons and the peaks at 1.62 ppm corresponding to the —$CH_2C\mathbf{H}_2C\mathbf{H}_2CH_2O$— protons are also observed. Compared with the spectrum of PTMG, a new signal at 2.03 ppm corresponding to the —$COC\mathbf{H}_3$ protons is observed in spectrum of acetylated PTMG.

As shown in Fig. 5 the ^{13}C-NMR spectrum of the native PTMG substantially corresponds to those of acetylated PTMG. The signals at 26.4 ppm arise from —$CH_2\mathbf{C}H_2\mathbf{C}H_2CH_2O$— carbons. The methylene carbons (adjacent to oxygen) give a signal at 70.7 ppm. Evidently, in spectrum of acetylated PTMG, the occurrence of two signals at 20.7 and 170.7 ppm characteristic of methyl group of an aliphatic acetyl group and carbonyl group in esterified acetyl group indicates the presence of —$OCOCH_3$ groups in the modified PTMG.

CONCLUSIONS

The acetylation reaction of PTMG by means of acetic anhydride in pyridine is an elegant method to protect hydroxyl groups of PTMG totally. The influence of various parameters on the extent of acetylation was studied. It was found that acetylation yield increases with the increment of reaction time, reaction temperature, and Ac_2O/OH molar ratio. Totally acetylated PTMG was obtained at 115°C for 4 h with Ac_2O/OH ratio equal to 4. More significantly, the totally acetylated PTMG can be used as chemical intermediate, and it can graft HFP to introduce fluorine into polyether glycol. After the grafting product was treated in 15% HCl, the hydroxyl groups could be regenerated. As a result, a new fluorinated polyether glycol was generated.

References

1. Park, Y. H.; Cho, C. G. J Appl Polym Sci 2001, 79, 2067.
2. Wu, Q.; Xu, J. J.; Yu, Y. Z. J Appl Polym Sci 2001, 80, 1237.
3. Chen, W. C.; Chen, H. H.; Wen, T. C.; Digar, M.; Gopalan, A. J Appl Polym Sci 2004, 91, 1154.
4. Kang, I. K.; Baek, D. K.; Lee, Y. M.; Sung, Y. K. J Polym Sci Polym Chem Ed 1998, 36, 2331.
5. Lin, M. F.; Shu, Y. C.; Tsen, W. C.; Chuang, F. S. Polym Int 1999, 48, 433.
6. Banu, P.; Radhakrishnan, G. Eur Polym J 2004, 40, 1887.
7. Rische, T.; Zschoche, S.; Komber, H. Macromol Chem Phys 1996, 197, 981.
8. Ünür, E.; Toppare, L.; Yagci, Y.; Yilmaz, F. Mater Chem Phys 2005, 91, 261.
9. Ge, Z.; Zhang, X. Y.; Dai, J. B. Eur Polym J 2006, 42, 395.
10. Fang, J. M.; Sun, R. C.; Tomkinson, J.; Fowler, P. Carbohyd Polym 2000, 41, 379.
11. Sun, X. F.; Sun, R. C.; Sun, J. X. Bioresource Technol 2004, 95, 343.
12. Rowell, R. M. Forest Prod J 2006, 56, 4.
13. Khalil, M. I.; Hashem, A.; Hebeish, A. Starch Stärke 1995, 47, 394.
14. Hill, C. A. S.; Jones, D.; Strickland, G.; Cetin, N. S. Holzforschung 1998, 52, 623.