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Grafting of Hexafluoropropylene onto Polytetramethylene Glycol by Radical Reaction

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Abstract: A well-defined modification of polytetramethylene glycol (PTMG) was realized by radical grafting with hexafluoropropylene (HFP). The structure of grafted product was confirmed by means of IR, ^{1}H NMR and ^{13}C NMR. The effects of the amount of initiator, reaction time and temperature on the grafting HFP onto PTMG were investigated.

Keywords: Radical grafting, polytetramethylene glycol, fluoropolymers.

Fluoropolymers exhibit a unique combination of high thermal stability, chemical resistance (to acids, bases and solvents), resistance to aging, low water absorptivity and attractive surface properties[1]. Therefore, they can be used in numerous applications such as aerospace, water repellent textile finishing and engineering[2], and there is a continuous demand in the synthesis of novel fluoropolymers. Fluorinated polyether glycols are particularly valuable fluoropolymers. They are generally prepared by copolymerization of fluorinated vinyl ether alcohols with fluorinated diols[3] or by photoxidative polymerization of tetrafluoroethylene and the subsequent thermal and chemical treatment of resulting product[4]. In this letter, we report a new synthetic method of fluorinated polyether glycol PTMG-*g*-HFP by performing a radical way of grafting hexafluoropropylene (HFP) onto polytetramethylene glycol (PTMG). PTMG is often used as chemical intermediate of polycondensate such as polyester and polyurethane. The chemical modification of PTMG by grafting HFP can extend the application of PTMG. The reaction process is very simple, easily controlled and reaction materials are inexpensive. Therefore, it is hopeful that the reaction can be applied to commercial use.

Grafting reaction was carried out in a 500 mL autoclave fitted with a stirrer, pressure gauge, bursting disc and inlet/outlet valve. In a typical reaction, 140 g molten PTMG (M_n=1000) and 0.0164 mol di-*tert*-butyl peroxide (DTBP) were charged. The reaction vessel was closed, frozen in an acetone/liquid nitrogen mixture until -70°C. Then 350 g HFP was introduced. The grafting reactions were carried out for various

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time at different temperatures. After completion of reaction, the autoclave was cooled to room temperature. The product was collected and purified by distillation under reduced pressure. The grafting percentage was calculated using the following equation:

$$GP(\%) = \frac{\text{PTMG - } g \text{ - HTP(g)} - \text{PTMG(g)}}{\text{PTMG(g)}} \times 100$$

In order to optimize the conditions for grafting, the effects of the amount of initiator, reaction time and temperature on the reaction are investigated. The results are used to evaluate grafting percentage. As shown in group 1 of **Table 1**, the grafting percentage increased with the increase of [DTBP]/[PTMG] (molar ratio) initially and then decreased. When the molar ratio is 0.12, GP reached the maximum. From the data shown in group 2, it can be seen that GP rose rapidly in the first 6 h, and then increased slowly. Group 3 shows that 140 °C is the rather efficient reaction temperature for this reaction.

Table 1 Effect of reaction condition on the grafting of PTMG onto HFP

Group	No.	[DTBP] / [PTMG]	Temperature (°C)	Time (h)	GP (%)
1	1	0.06	140	6	50
	2	0.08	140	6	94
	3	0.10	140	6	127
	4	0.12	140	6	141
	5	0.14	140	6	122
	6	0.16	140	6	82
2	7	0.12	140	2	55
	8	0.12	140	4	108
	9	0.12	140	6	141
	10	0.12	140	8	143
3	11	0.12	110	6	59
	12	0.12	120	6	86
	13	0.12	130	6	104
	14	0.12	140	6	141

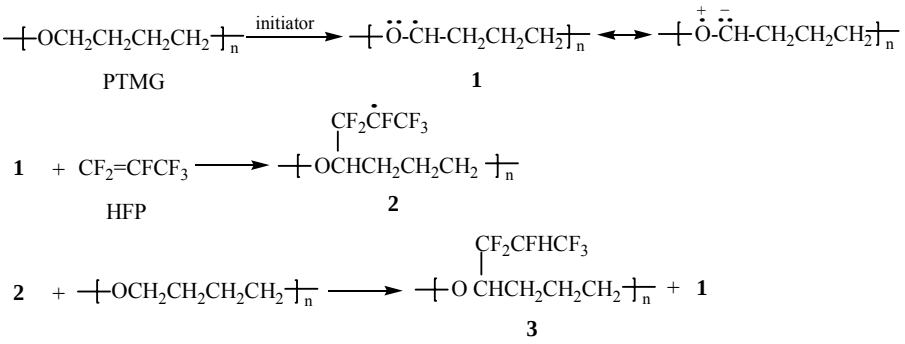
Structural modification was evidenced by the IR spectrum of PTMG-*g*-HFP, in which there were new absorption bands dealing with the vibration absorption of C-F bond except all the characteristic absorption bands of PTMG. The stronger characteristic absorption bands locating at 1190 cm^{-1} and 1287 cm^{-1} can be attributed to stretching vibrations of C-F[5]. The absorption bands at 839 cm^{-1} and 680 cm^{-1} are resulted from the stretching vibration of CF_3 and deformation vibration of CF_2, respectively[6]. In addition, the absorption band at 1106 cm^{-1} originated from C-O-C group of PTMG shifted to a high value of 1115 cm^{-1} and became weaker in the spectrum of PTMG-*g*-HFP. This showed that the grafting reaction was occurred at the carbon of the ether link.

^{1}H NMR analysis further supported the chemical structure of PTMG-*g*-HFP. Several peaks for the fluoromethenyl protons ($-CF_2CFHCF_3$) appeared from 4.64 ppm to 5.15 ppm, and the peaks assigned to the methenyl protons ($-CF_2CHO-$) appeared at 3.65 ppm. The occurrence of grafting reaction was also evidenced by the corresponding ^{13}C NMR spectrum of PTMG-*g*-HFP. Some peaks between 84 ppm and 88 ppm

corresponded to **C**FH-CF_3. The peaks centered at 122 ppm was assigned to -CF_2-**C**F_3. The presence of the CF_2 group adjacent to the methenyl group was evidenced by the peak at 119 ppm[7]. The peaks centered at 76 ppm was assigned to –CH-O-. All these evidence showed that the new group (-CF_2CFHCF_3) was generated in the grafting reaction [8-9].

The whole reaction process is depicted in **Scheme 1**. PTMG initiated by initiator can generate nucleophilic radical **1**. Radical **2** can be formed by the reaction of radical **1** with HFP. The resultant radical **2** is electrophilic and therefore abstracted a hydrogen atom from the relatively electron-rich C-H site (adjacent to oxygen in PTMG), giving product **3**, which was fluorinated polyether glycol PTMG-*g*-HFP and regenerating radical **1**.

Scheme 1



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