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# Synthesis, characterization and properties of a novel fluorinated polyurethane

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ABSTRACT

A novel fluorinated polyurethane (FPU) was prepared by fluorinated polyether glycol (PTMG-*g*-HFP) as a soft segment, 1,6-hexamethylene diisocyanate (HDI) or toluene diisocyanate (TDI) as a hard segment and 1,4-butanodiol (BDO) as a chain extender. Fourier transform infrared spectroscopy (FTIR), $^{1}$H NMR, $^{13}$C NMR and gel permeation chromatography (GPC) were used to characterize the structure of the fluorinated polyurethane. The thermal stabilities of the fluorinated polyurethane and the corresponding hydrogenated polyurethane were studied by thermogravimetric analysis (TGA). X-ray photoelectron spectroscopy (XPS) analysis at two different sampling depths for the fluorinated polyurethane was used to investigate the surface compositions of FPU. And the mechanical properties of the fluorinated polyurethane and the corresponding hydrogenated polyurethane were also measured. Chemical resistance of polyurethane films was estimated through spot tests with different solvents. The results showed that FPU had high thermal stability, strain-hardening property and good chemical resistance. The XPS measurements showed the fluorine enrichment on the surface of FPU.

## 1. Introduction

Fluorinated polyurethane is a new class of functional materials. It combines some virtues of polyurethane and fluorinated polymer, such as high thermal stability, good chemical resistance (to acids, bases and solvents), low water absorptivity and attractive surface properties, excellent resistance to ultraviolet radiation and nuclear radiation, excellent flexibility, good wearability and high weatherability [1–7]. Therefore, the study of fluorinated polyurethane has been attracted considerable interest in recent years.

Fluorocarbon chains have been incorporated into polyurethanes by fluorinated diisocyanates [8], chain extenders [9–11], polyether glycols [12–15], polyester glycols [16] and end-cappers [17–18]. For instance, Tang first prepared NCO-terminated prepolymer, and then the prepolymer was end-capped with fluorinated alcohol [17]. Ratner synthesized a series of fluorinated polyurethanes by using various fluorinated chain extenders and studied their properties [7]. Tonelli et al. [12] used perfluoropolyether glycol (PFPE) as a soft segment to prepare fluorinated polyurethane, which had high thermal stability and good chemical resistance. However, because of the higher synthesizing cost and fewer varieties of fluorinated diisocyanates, the synthesizing route of fluorinated polyurethane with fluorinated diisocyanates was often not used. Owing to the less fluorine content and lower molecular weight of fluorinated alcohols, the improvement of properties of fluorinated polyurethane prepared by fluorinated alcohol as end-capper was not evident compared with hydrogenated polyurethane. There are also some problems with the synthesis of fluorinated polyurethane using fluorinated extenders. These extenders, because of their low molecular weights, do not present the improvement of properties [2]. Now, fluorinated polyurethane was mostly synthesized by

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fluorinated macromolecular diols as soft segments. The fluorinated groups of the macromolecular diols used are mainly distributed in the main chains. Ameduri et al. [19] proposed that the surface properties of fluorinated materials with fluorine-containing pendent groups were better than those with fluorinated groups in the main chains. But the fluorinated polyurethane was seldom synthesized by macromolecular diols as soft segment with fluorine-containing pendent groups.

In our previous works, a new fluorinated polyether glycol (PTMG-*g*-HFP) with fluorinated pendant groups was synthesized by radical grafting reaction [20–22]. In this paper, we report a novel fluorinated polyurethane (FPU) was synthesized using PTMG-*g*-HFP as chemical intermediates. The structure of the novel fluorinated polyurethane was confirmed by FTIR, $^1$H NMR and $^{13}$C NMR. The surface composition of the novel fluorinated polyurethane was investigated by XPS. At the same time, chemical resistance was also measured.

## 2. Experimental

### 2.1. Materials

Polytetramethylene glycol (PTMG, $M_n = 1500$) was purchased from Mitsubishi Chemical and dried under a reduced pressure at 80 °C for 4 h before use. PTMG-*g*-HFP (FPTMG, $M_n = 1500$) was prepared according to the method of our publications [20–22] and vacuum-dried before reaction. The structure of PTMG-*g*-HFP was fully characterized in the previous works [20–22]. PTMG-*g*-HFP spectroscopic data: FTIR/cm$^{-1}$: 3467 (OH stretching), 2940, 2857, 1430 and 1368 ($CH_2$ and CH stretching), 1115 (C—O stretching), 1190 and 1287 (C—F stretching), 839 ($CF_3$ stretching), 680 ($CF_2$ deformation); $^1$H NMR/ppm ($CDCl_3$): 4.64–5.15 (m, 1H, $CF_2CF\mathbf{H}CF_3$), 3.65 (s, 1H, $CF_2C\mathbf{H}O$), 3.86 (s, 1H, $O\mathbf{H}$), 1.6–1.8 (m, 4H, $CH_2C\mathbf{H}_2CH_2$), 1.9–2.2 (m, 1H, $CH_2C\mathbf{H}_2CH$), 3.43 (m, 2H, $C\mathbf{H}_2O$). 1,6-hexamethylene diisocyanate (HDI, Aldrich) and toluene diisocyanate (TDI, Bayer) were used as received. Dibutyltindilautrate (DBTDL), 1,4-butanodiol (BDO), acetone (AC) and butanone were purchased from China Medicine, Shanghai Chemical Reagent Corporation. BDO was distilled under vacuum from calcium hydride and then dried over 4 Å molecular sieves prior to use. All the materials above mentioned were used without further purification unless otherwise specified.

### 2.2. Synthesis of fluorinated polyurethanes and hydrogenated polyurethanes

Fluorinated polyurethanes (FPU) were prepared by a two-step solution polymerization method. The diisocyanate with the stoichiometric amount was dissolved in butanone. The solution was stirred at 90 ± 2 °C under a dry nitrogen atmosphere and FPTMG was fed dropwise in 2 h. The reaction mixture was kept for another 2 h at 90 ± 2 °C. The chain extender (BDO) with the calculated amount and 0.1 wt% DBTDL were added to the reaction solution while the temperature was kept at 75–80 °C for 2 h. The reaction completion was monitored by the absence of IR-absorption of the free NCO group at 2270 cm$^{-1}$. The whole reaction process is depicted in Fig. 1.

Hydrogenated polyurethanes were also prepared for the comparison purpose. The synthesizing process and reaction conditions of the hydrogenated polyurethanes were almost the same as those of the fluorinated polyurethanes, except using PTMG as soft segment.

### 2.3. Film preparation

PU and FPU films were prepared by casting from a 10 wt% AC solution onto glass plates, drying at 60 °C for 48 h, followed by further drying in a vacuum oven at 60 °C for 72 h to remove any residual solvent, and then stored in a desiccator to avoid moisture.

### 2.4. Measurements

Infrared spectra were obtained on a Bruker Equinox 55 FTIR spectrometer in the 4 cm$^{-1}$ resolution mode. Sixteen

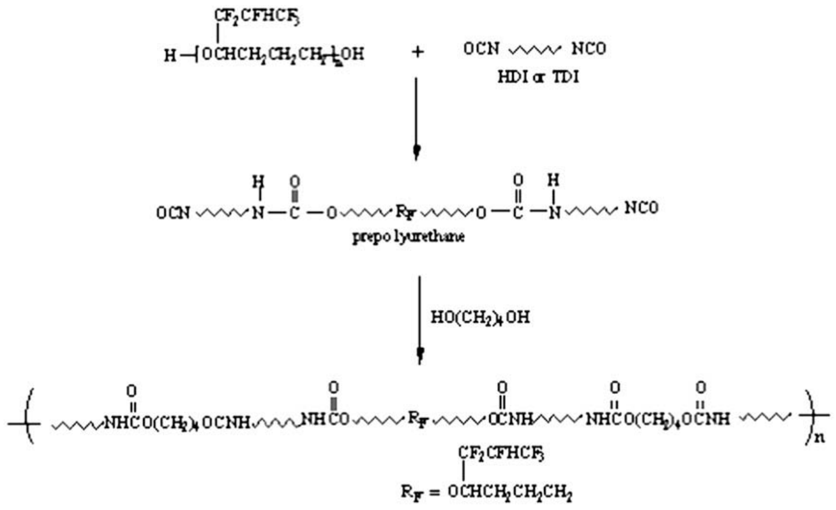

**Fig. 1.** Reaction scheme of FPU copolymer.