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Preparation of fluoropolymer with gem-bis-fluoroalkylated side-chain and its’ application on cotton fabric finishing

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Abstract: In this study, three types of fluorinated polyacrylates (PBFB, PBFS and PMFA) were synthesized by 4-gem-bis(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1-butene, 4-gem-bis(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-methine-1-styrene, and 3,3,4,4,5,5,6,6,6-nonafluorohexyl acrylate respectively as monomers via emulsion polymerization. Particle size, particle size distribution and zeta potential were tested to assess the emulsion stability. Afterwards, the latexes were coated onto fabrics to obtain gem-bis(fluoroalkyl)-cotton. The surface properties of the treated cotton fabrics were analyzed by X-ray photoelectron spectroscopy and water contact angle. It was found that, when controlling the fluorine content level to be similar, WCAs of gem-bis(fluoroalkyl)-cottons was 127±0.5 ° and 134.9±0.7 ° respectively, which were both higher than that of mono-fluoroalkyl-cotton (PMFA-cotton of 125.2±0.2 °). This showed that gem-bis-fluoroalkyl groups could provide better hydrophobic performance than mono-fluoroalkyl group, especially when the rigid benzene was used as a side-chain bridged group.

Keywords: Fluorinated polyacrylate; Emulsion polymerization; Waterproof property; Gem-bis-fluoroalkyl

Introduction

Fluorinated polyacrylates have been widely used in textile, leather and paper industry due to a number of properties, such as low surface energy, high thermal stability, excellent film-forming
property, corrosion resistance, hydrophobicity and oleophobicity \(^1\text{-}^5\), etc. They can be synthesized via conventional emulsion polymerization, suspension emulsion polymerization, seed emulsion polymerization and solvent polymerization \(^6\text{-}^{10}\), in which conventional emulsion polymerization processes are most commonly used.

The excellent hydrophobic and oleophobic properties of fluoropolyacrylate depend on the flexibility of the polymer backbone, the length of the fluoroalkyl chains, and the bridging group between the backbone and the fluoroalkyl side chain \(^11\text{-}^{15}\). However, fluoropolymers with long-chain fluoroalkyl side-groups are difficult to hydrolyze or biodegrade under most environmental conditions, which cause a series of problems to daily life and the environment \(^16\). Perfluorocarbon chains contain more than eight carbons possess long biological half-lives, bioaccumulate in human, animal tissue and resist degradation \(^17\). Fortunately, it was found that the toxicity and bioaccumulation of the fluoroalkyl groups decrease dramatically with the decrease of carbon atoms in the fluoroalkyl group \(^18\). Therefore, research and development of short-chain fluoroalkyl functional materials with similar surface energy to long-chain fluoroalkyl products have become extremely meaningful.

In this study, gem-fluoroalkyl monomers with different bridging groups were synthesized as 4-Gem-bis(2,2,3,3,4,4,5,5,5-nonafluoropentyl) -1-butene and 4-Gem-bis(2,2,3,3,4,4,5,5,5-nonafluoropentyl) -methine-1-styrene (Scheme 1). Afterwards, two novel short-chain gem-bis-fluoroalkylated polymers (PBFB and PBFS) were prepared by emulsion co-polymerization with stearyl acrylate, butyl acrylate and hydroxyethyl methacrylate. The latexes were then coated onto fabric to obtain gem-bis(fluoroalkyl)-cotton, and properties of
the finished cotton fabric were lastly studied. A control co-polymer was prepared using 3,3,4,4,5,5,6,6,6-nonafluorohexyl acrylate as mono-fluoroalkyl monomer (Scheme 2).

**Experimental**

**Materials**

3,3,4,4,5,5,6,6,6-nonafluorohexyl acrylate acrylate was supplied by Shanghai qinba chemical Co., Ltd. Stearyl acrylate (SA), butyl acrylate (BA), hydroxyethyl methacrylate (HEMA), magnesium sulfate (MgSO₄), methanol and ether were purchased from Jiangsu Yonghua Chemistry Co., Ltd. Pd(dppf)Cl₂CH₂Cl₂ was supplied by Suzhou argon krypton xenon trade Co., Ltd. Sodium dodecyl sulfate (SDS) and alkyl alcohol polyoxyethylene ether (AEO-9) were obtained from Aladdin Chemistry Co., Ltd. Ammonium persulfate (AP) and copper bromide (CuBr) were supplied by Shanghai Titan Technology Co., Ltd. All of these above were used without further purification. Tetrahydrofuran (THF) offered by Qiangsheng Functional Chemicals Co., Ltd was purified by distillation. The water utilized in this experiment was deionized.

**Synthesis of 4-gem-bis(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1-butene (A)**

1,3-Perfluoro-n-butyl-2-iodo-propane (6.30 g, 10.40 mmol), Pd(dppf)Cl₂CH₂Cl₂ (0.25 g, 0.30 mmol) and THF (16ml) were taken into a stirred flask under nitrogen atmosphere. After the mixture was cooled to 0°C, the prepared Grignard reagent solution (14.60 ml, 14.60 mmol) was added drop-wise for 2 h. The mixture was then transferred to room temperature (Green color) and stirred for another 16 h. After the reaction was completed, the reactants were quenched with 8 ml
methanol. Then the oil layer was separated and extensively washed with water and 4.86 g of pure product was obtained after removal of solvent under reduced pressure (90% yield).

**Synthesis of 4-Gem-bis(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-methine-1-styrene (B)**

1,3-Perfluoro-n-butyl-2-iodo-propane (2.08 g, 3.44 mmol), CuBr (0.028 g, 0.19 mmol) and THF (25 ml) were placed in a 50 ml flask, stirred vigorously and heated to 60°C. The prepared Grignard reagent solution was added drop-wise in 4h, the mixture turned yellow in a few seconds. After that, the reaction was kept for 20 h at room temperature. After completion of the reaction, it was quenched with saturated brine and extracted with 50 ml ether for three times. The organic phases were combined and extensively washed with water, then dried with anhydrous magnesium sulfate. After removal of solvent under reduced pressure, 1.26 g of product was obtained with 63% yield.

**Preparation of Fluorinated Co-polymer**

Emulsion co-polymerization was carried out by using BA, SA, HEMA as mixed monomers, and compound A, B and 3,3,4,4,5,5,6,6,6-nonafluorohexyl acrylate as fluorinated functional monomers.

Emulsifiers were AEO-9 and SDS, consumption was both 1.5% of the total mass of monomers. The recipes were listed in Table 1. The monomers and emulsifiers were pre-emulsified for 15 min with a speed of 8000r/min. Then, the pre-emulsion was transferred into a three-necked round bottle and heated to 70°C under N₂ atmosphere. A solution of AP in 5 ml de-ionized water was added drop-wise into the pre-emulsion within 30 min to initiate the reaction. The polymerization was kept for another 3 h at 70°C. Finally, the products were filtered to remove the coagula to
obtain latexes.

Application of the Fluorinated Co-polymer Latexes on Cotton Fabrics

Latexes were dissolved in de-ionized water to form 80 g/L finishing agent. The desized cotton fabrics were immersed in the emulsion for 30 min, and padded through two-dips and two-nips with a wit pick-up of 80%, dried at 90°C for 3 min and cured at 160°C for 2 min. Finally, the cotton fabrics coated with PBFB (named as PBFB-cotton), PBFS (PBFS-cotton) and PMFA (PMFA-cotton) were kept in a desiccator to balance at room temperature for 24 h.

Characterization

$^1$H NMR spectra were recorded on an INOVA-400MHz NMR spectrometer in deuterated chloroform (CDCl$_3$) with TMS as internal standard. Fourier transform Infrared spectroscopy (FT-IR) spectra were recorded using a Nicolet 5700 spectrometer at 4 cm$^{-1}$ resolution (KBr disks). The particle size and zeta potential were obtained by using a Mastersizer 2000 particle sizer. Surface chemical compositions of cotton fabrics were analyzed by X-ray photoelectron spectroscopy (XPS) measurement on Axis Ultra HAS photoelectron spectrometer, which equipped with monochromatic Al Kα X-ray source. The surface morphology of the cotton fabrics before and after finishing were observed by TM 3030 Scanning Electron Microscope. Thermal-gravimetric analysis (TGA) was conducted on a Diamond 5700 thermal analyzer under the nitrogen atmosphere at a heating rate of 10 °C/min. Static water contact angles (WCAs) of the treated fabrics were measured by Dataphysics OCAH200 at room temperature. The injection volume of liquid was 3μL and the value was the average of three separate measurements made on different areas.
Results and Discussion

Structure Characterization of Fluorinated Monomers and Fluorinated Co-polymers

Three types of fluoroalkylated co-polymer were prepared by emulsion polymerization. The chemical structures of synthesized products were confirmed by $^1$H NMR. Figure 1 and Figure 2 presented the $^1$H NMR spectra of gem-bis-fluorinated monomers. The structures of 4-gem-bis(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1-butene and its polymer film were further confirmed by FT-IR as shown in Figure 3. It can be seen that both the monomer and polymer exhibited the stretching vibrations of C-H at 2925.4 cm$^{-1}$ and 2855.0 cm$^{-1}$. The absorption peaks at 1355.9, 1239.8 and 1134.8 cm$^{-1}$ were assigned to the stretching vibration of C-F bond. Compared with the infrared spectrum of the fluorinated monomer (a), there was no peak found in curve (b) at 1644.5 cm$^{-1}$ which was attributed to the vibration of C=C, while a new appeared stretching vibration of C=O indicated that the monomer had participated in the emulsion polymerization.

The structures of 4-gem-bis(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-methine-1-styrene and its polymer film were identified by FT-IR (Figure 4), where 2931.1 cm$^{-1}$ and 2842.6 cm$^{-1}$ can be ascribed to the symmetric stretching vibration of C-H and the absorption peaks at 1350.9 cm$^{-1}$, 1286.9 cm$^{-1}$ and 1132.5 cm$^{-1}$ corresponded to the stretching vibration of C-F. In the spectrum of the polymer film (d), strong peak at 1717.2 cm$^{-1}$ ascribed to the vibration of C=O. Furthermore, the absorption peaks at 1633.2 cm$^{-1}$ assigned to C=C completely disappeared, confirming the successful copolymerization of fluorostyrene monomer. As shown in Figure 5, both 3,3,4,4,5,5,6,6,6-nonafluorohexyl acrylate and its polymer exhibited the stretching vibration of
C-H at 2915.8 cm\(^{-1}\) and characteristic absorption peak of C=O stretching vibration at 1733.1 cm\(^{-1}\).

Moreover, the characteristic stretching vibration of C-F bond appeared at 1236.7 cm\(^{-1}\), 1187.1 cm\(^{-1}\), 1131.1 cm\(^{-1}\).

**Particle Size and Zeta Potential of Fluorinated Polyacrylate Latexes**

Particle size is a representation of the emulsion stability. The average particle size (with same fluorine content) of PMFA, PBFB and PBFS were 253.7 nm, 261.7 nm and 316.1 nm, respectively. Obviously, the particle size of gem-bis-fluoroalkylated co-polymer was larger than that of mono-fluoroalkyl co-polymer. This is because of the stronger hydrophobic interactions around the particles of gem-bis-fluoroalkyl and the induced aggregation of particles\(^{19}\). PDI test illustrated that two gem-bis-fluoroalkyl co-polymer emulsion particles were uniformly distributed (Figure 6). Figure 7 presented the particle size distribution of PMFA latex with different fluoroalkyl molar. It’s clearly that the distribution became broader and the values of PDI increased gradually with the increment of fluorine content, which revealed poor dispersibility of PMFA with high fluorine content.

Zeta potential result was consistent with particle size distribution and the stability of the obtained emulsion. The zeta potential of PBFB and PBFS were -57.8 mV and -52.4 mV, respectively. Highly absolute value means that the latex particles tend to disperse due to charge repulsion\(^{20}\) and the emulsion system was stable. With the increase of fluoroalkyl molar content, the zeta potential absolute values of PMFA decreased (PMFA-1: -52.8 mV; PMFA-2: -51.5 mV; PMFA-3: -48.3 mV), demonstrating that the stability of mono-fluoroalkyl co-polymer latexes decreased with the increase of fluorine content.
X-ray Photoelectron Spectroscopy

The surface chemical element of cotton fabrics before treatment and after coated with PBFB, PBFS and PMFA were characterized by X-ray photoelectron spectroscopy (XPS). Chemical composition changes of cotton fabric before and after finishing were shown in Figure 8. As it can be seen, the strong characteristic signal of carbon and oxygen appeared at 282 eV and 528 eV, respectively. Furthermore, compared with the spectrum of pristine cotton, strong peaks with binding energy of 684 eV which attributed to F₁s were found in the spectra of coated samples (b, c and d). This demonstrated that the surface of the treated cotton fabrics were covered by fluoropolymer films.

Surface Morphology of Fluorinated Co-polymer Film on Cotton Substrates

It is widely accepted that during the finishing process, co-polymers crosslink on the fiber, forming films and covering the surface. Thus, morphology of the treated fabric should be observed to further identify the deposition of latexes. The surface morphology of the cotton fabric before and after finishing was tested by scanning electron microscopy (SEM). As shown in Figure 9, surface of pristine cotton was uneven and the typical longitudinal fibril structure with natural veins could be observed, while the surfaces of PBFB-cotton, PBFS-cotton and PMFA-cotton became smooth and the slender concave grooves fully disappeared. The results implied that fluorinated co-polymers were successfully coated onto the surface of cotton fibers.

Thermal properties Analysis

Thermal properties of cotton fiber improved after treatment with fluoropolymer. In this study, PBFB-cotton, PBFS-cotton and PMFA-cotton were evaluated by thermo-gravimetric analysis
(TGA) under a nitrogen atmosphere, and the results were included in Figure 10. As can be seen, there were three decomposition stages for all the cotton fibers. The initial decomposition temperature of pristine cotton was 292°C, while the values increased to 300°C, 316°C and 320°C after finished with PBFB, PBFS and PMFA, respectively. Afterwards, all the cotton fibers underwent the stage of rapid weight loss, which was corresponding to the deposition of carbon chains with a losing rate up to 70%. At the ending decomposition stage, the pristine cotton completely decomposed at 372°C, whereas the cotton fabric finished with PBFB, PBFS and PMFA decomposed more slowly and completely decomposed only when the temperature reached 381°C, 386°C and 389°C, respectively. This indicated that the thermal stability of the cotton fibers improved after coated with fluoropolymer, which possessed the tightly bonded C-F bond in fluoroalkyl side-chains.

**Water Contact Angles of Cotton Fabrics Coated with Fluorinated Co-polymers**

In the finishing process, the fluoroalkyl groups migrated towards air under high temperature to minimize the surface free energy of fabrics. In the present work, water contact angles (WCAs) were measured to evaluate the surface properties of treated cotton fabrics. It can be seen in Figure 11 that the WCAs of cotton fabrics finished with PBFB and PBFS were 127.7±0.5 ° and 134.9±0.7 °, respectively. Both of them were larger than the one of PMFA-cotton(125.2±0.2 °) even when the fluorine content of fluoropolymer treating agent was similar. This is because that the structure of the gem-bis-fluoroalkyl was more rigid than the mono-fluoroalkyl side-chain, and the resultant orderly arrangement of the fluoroalkyl groups on the surface of substrate materials provided lower surface free energy. In addition, the water contact angle of PBFS-cotton was
higher than PBFB-cotton, indicating that the introduction of rigid benzene group was conducive to the orientation of end-bonded fluoroalkyl side-chain and thus reduced the surface free energy. A commercially available short-chain fluoroalkyl water repellent finishing agent 3622 (manufactured by 3M China) was used in the same process to prepare the 3622-cotton and the WCA was listed in Figure 11(f), whose water repellent performance was excellent, while inferior to PBFS-cotton.

The water contact angles (WCAs) of PMFA-cotton increased with the increment of fluorine content of treating agent. Only when the molar amount of mono-fluoroalkyl attaching on the main-chain was three times (Fig.11 c) of that of gem-bis-alkyl groups (Fig.11 e), the WCAs of the two coated cotton fabrics reached the same level.

**Conclusion**

Two novel gem-bis-fluoroalkylated monomers with different bridging groups were successfully synthesized and characterized by FT-IR. Afterwards, the corresponding fluorinated co-polymeric latexes were prepared by emulsion co-polymerization and then coated on cotton fabrics. It was confirmed that the latexes were uniform and stable by particle sizes and zeta potential test. XPS and SEM analysis indicated that fluorinated co-polymers have been coated on the surface of cotton fibers. The thermal stability of cotton improved after finishing. Furthermore, the treated cotton fabrics were identified to be water-repellent and the WCAs of cotton fabrics finished with PBFB and PBFS were higher than that of PMFA-cotton at the same fluorine content level of fluoropolymer, demonstrating that the structure of the rigid gem-bis-fluoroalkyl were conducive to the orientation of side-chain fluoroalkyl groups and thus reduced the surface free
energy of treated fabrics. The water repellency could be furtherly improved by introducing the rigid benzene as a bridging group between the polymer main-chain and side-group.

**Acknowledgements**

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Scheme 1. Synthesis of gem-bis-fluorinated monomers.

Scheme 2. Synthetic route of fluorinated polyacrylates.

Table 1. Recipes for the preparation of fluorinated polyacrylates

Figure 1. $^1$H NMR spectrum of 4-gem-bis(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1-butene.

Figure 2. $^1$H NMR spectrum of 4-gem-bis(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-methine-1-styrene.

Figure 3. FT-IR spectra of 4-gem-bis(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1-butene (a) and the polymer PBFB (b).

Figure 4. FT-IR spectra of 4-gem-bis(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-methine-1-styrene (c) and its polymer PBFS (d).
Figure 5. FT-IR spectra of 3,3,4,4,5,5,6,6,6-nonafluorohexyl acrylate (e) and its polymer PMFA (f).

Figure 6. The particle size distribution of latexes: (a) PBFB, (b) PBFS, (c) PMFA.

Figure 7. The particle size distribution of PMFA latex with different fluorine content.

Figure 8. The XPS pattern of cotton fabric before and after finishing: (a) pristine cotton, (b) PMFA-cotton, (c) PBFB-cotton, (d) PBFS-cotton.

Figure 9. SEM images of cotton fibers: (a) pristine cotton, (b) PMFA-cotton, (c) PBFB-cotton, (d) PBFS-cotton.

Figure 10. TGA curves of pristine cotton and coated cotton.

Figure 11. Water contact angles of cotton fabrics coated with fluoropolymer: (a) PMFA-1, (b) PMFA-2, (c) PMFA-3, (d) PABFB-cotton, (e) PABFS-cotton, (f) 3622-cotton.
Scheme 1. Synthesis of gem-bis-fluorinated monomers.

125x103mm (300 x 300 DPI)
Scheme 2. Synthetic route of fluorinated polyacrylates.

144x178mm (300 x 300 DPI)
Figure 1. 1H NMR spectrum of 4-gem-bis(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1-butene.

143x100mm (96 x 96 DPI)
Figure 2. $^1$H NMR spectrum of 4-gem-bis(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-methine-1-styrene.
Figure 3. FT-IR spectra of 4-gem-bis(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1-butene (a) and the polymer PBFB (b).
Figure 4. FT-IR spectra of 4-gem-bis(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-methine-1-styrene (c) and its polymer PBFS (d).

287x201mm (300 x 300 DPI)
Figure 5. FT-IR spectra of 3,3,4,4,5,5,6,6,6-nonafluorohexyl acrylate (e) and its polymer PMFA (f).

Wavenumber(cm⁻¹)

288x200mm (300 x 300 DPI)
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279x215mm (300 x 300 DPI)
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