Study on Preparation of Fluorinated Photosensitive Copolymer and Surface Wettability Light Regulation

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Abstract. Low surface energy and micro/nano structure are two key factors affecting the construction of hydrophobic surfaces. In this paper, a series of tetrafluoropropyl methacrylate (TFPMA) and 6-[-4-[(trifluoromethoxy)phenyl]diazenyl]phenoxy]hexyl acrylate (FAzo) random copolymer [P(TFPMA-co-FAzo)] of different monomer molar ratios were prepared by free radical solution polymerization; and the chemical structure of the copolymer was characterized in detail using FTIR and $^1$HNMR. The introduction of long-chain flexible acrylate components with high fluorine content can effectively reduce the surface energy of the material. When the molar ratio of TFPMA is increased to 70%, the static water contact angle on the surface of the copolymer film is increased to 90°. By doping 10 wt% micron-sized PTFE particles, the water contact angle on the surface of the copolymer film can be further increased to 105°; Meanwhile, based on the cis-trans isomerization reaction of the azobenzene component in the copolymer, light irradiation with different wavelengths can realize the rapid and reversible regulation of hydrophobic/hydrophilic properties on the surface of copolymer film. This method of combining low surface energy fluorine-containing component with photosensitive azobenzene to construct light-responsive hydrophobic surface has a good research prospect.

Keywords. Azobenzene, fluorinated acrylate, surface modification, hydrophobic surface.

1. Introduction
Intelligent response materials have attracted wide attention due to their applications in biosensors [1], microfluidic devices [2], and smart membranes [3]. Today, temperature [4], magnetic field [5, 6], pH [7, 8], and light [9-11] various stimuli responsive smart materials responsive are widely developed and used. Among them, light for its advantages of avoiding secondary pollution caused by contact with the sample, strong responsiveness and high spatial resolution, has grabbed researchers’ attention in surface wettability control [12]. At present, a large number of inorganic transition metal oxides are used to study the wettability control of the film surface, such as: ZnO [13, 14], SnO$_2$ [15], Fe$_2$O$_3$ [16], TiO$_2$ [17-19], V$_2$O$_5$ [20], WO$_3$ [21] etc., but the surface wettability and photosresponse of these inorganic transition metal oxide films are slow, and the hydrophobic/hydrophilic transition takes hours or even days [22]. Azobenzene organic materials have become the focus of research in this field due to their rapid cis-trans isomerization reaction under light irradiation. Azobenzene will change from trans-structure to cis-structure under ultraviolet (UV) irradiation. Under the condition of visible light (Vis) or heating, it will quickly recover from cis-structure to trans-structure. During the reversible
cis-trans isomerization of azobenzene, there are significant changes in molecular structure size and dipole moment (polarity) (0.5-3.1 Debye), which makes it a unique advantage in the surface construction of photoresponsive materials [23]. In 2006, the research group of Kilwon Cho reported a optically controlled erasable super-wetted patterned material surface. Multilayer composite film of inorganic nano particles is constructed by electrostatic self-assembly, and small azo-containing molecules are modified on the surface. The surface can realize the reversible conversion from superhydrophobic to superhydrophilic state under different light irradiation; further, by selective exposure, it can realize the construction of multiple patterned super-wetted surfaces [24]. In 2012, the research group of Jurgen Ruhe built a polymer monomolecular film containing trifluoromethoxy azobenzene side groups on a silicon substrate with spin-coating technology. This monomolecular film has good light-controllability and can achieve a reversible conversion from highly hydrophobic to superhydrophilic (134°-0°) [10]. In 2014, the research group of Zhang Weidong and Hu Zhijun modified the surface of silica nanoparticles by spin-coating with trifluoromethoxyazobenzene characteristic groups, and achieved a reversible change in water contact angle of 16° on the surface of the film under light control. The method is simple and efficient, but the variation of interface wettability is relatively small [25].

The addition of soft monomers to the polymer chain can effectively adjust the flexibility and surface properties of the copolymer. The introduction of flexible acrylate monomers with long side chains can effectively improve the film-forming properties of the fluorinated copolymer while ensuring the high fluorine content of the copolymer. In addition, the introduction of stimuli-responsive components (such as azobenzene, spiropyran, etc.) into the structure of fluorocopolymers can realize the construction of intelligent super-wetted material surfaces. However, currently, the preparation of smart material surfaces with switchable super-wetted characteristics with high efficiency, low cost, and bulk production is still a challenging subject.

2. Experimental Section

2.1. Materials
2, 2, 3, 3-tetrafluoropropyl methacrylate (TFPMA, 98%) was purchased from Aladdin. 6-[4-[(4-(trifluoromethoxy)phenyl)diazoo]phenoxy]hexyl acrylate (FAzo) was homemade in the laboratory. 2,2-Azobisisobutyronitrile (AIBN, 98%) was purchased from Sigma-Aldrich and recrystallized twice from ethanol. PTFE (1-3μm) was purchased from Macleans.

2.2. Synthesis of Poly(TFPMA-co-FAzo)
P (TFPMA-co-FAzo) random copolymers with different molar ratios were synthesized by free radical solution polymerization. First, TFPMA/FAzo (10 g) monomers with different molar ratios were dissolved in N, N-dimethylformimine (DMF) (25 mL) under nitrogen protection, and 0.1 g of initiator AIBN was added and reacted at 80 °C for 24 hours. When the reaction was completed, the mixed solution was added dropwise to 200 ml of deionized water. The resulting precipitate was dissolved in THF and re-precipitated three times in deionized water. The resulting orange solid product was collected and dried in a vacuum oven at 30 °C for 48 hours. A homopolymer (Poly-Azo) containing azobenzene was synthesized by the same procedure as described above.

2.3 Fabrication of Glass-Based Smart Surfaces
Slides (20 × 20 mm) were purchased from Yancheng Huanghai Electronics Co., Ltd. (Yancheng, China). Using a glass slide as a substrate, a photosensitive polymer film was prepared by a simple spin coating method. First, the slides were sonicated with ethanol and acetone for 20 minutes. Then, it was boiled in a mixed solution of distilled water, ammonia water and hydrogen peroxide at 4: 1: 1 (volume ratio) at 80°C for 30 minutes, and the processed slide was placed in ethanol for use. Polymer THF doped with different proportions of PTFE was spin-coated on a glass substrate (2000 r/min). The polymer film prepared by spin coating was dried in a vacuum oven at 30 °C for 12 h.
2.4. Characterizations

The nuclear magnetic resonance spectrum was characterized with CDCl$_3$ used as a solvent by an Advance III 400 MHz NMR spectrometer (Bruker BioSpin, Karlsruhe). Infrared spectra were measured using a Nicolet Is10 FT-IR spectrophotometer (Thermo Fisher, USA). Gel permeation chromatography (GPC) (Waters 1500) with THF as the mobile phase was used to characterize the molecular weight and dispersion (D) of the target polymer. The UV-vis absorption spectrum of the polymer was measured by an ultraviolet-visible spectrophotometer TU-1901. Scanning electron microscope (SEM) (S-2500, Hitachi Seiki) was used to characterize the surface morphology and element distribution of the composite film. The surface wettability of the composite film was characterized by WCA measurement (OCA40, Dataphysics, Germany) at room temperature. 2μL of water droplets were dropped on the surface of the polymer film. After the droplet profile stabilized, the water contact angle was recorded and analyzed; the above operation was tested 5 times at different positions on the surface of the composite film, and the average value was taken. The ultraviolet and visible light intensities used were 80 mW/cm$^2$ and 200 mW/cm$^2$ (CEL-HXF300, CEAULIGHT). The light intensity was measured by an optical power meter (CEAULIGHT).

3. Results and Discussion

A series of azobenzene-containing random copolymers P(TFPMA-co-FAzo) were obtained by radical polymerization (figure 1a). The prepared azobenzene-containing random copolymers all have similar molecular weights (9000-11,000) and low PDI (1.14-1.54). The chemical structures of the copolymers with different comonomer molar ratios were characterized by $^1$H NMR, as shown in figure 1b. The characteristic peaks of (4H, Ar-H) -CH$_2$ on the benzene ring of azobenzene are 7.00 ppm, 7.49 ppm and 7.93 ppm, respectively [26]. The characteristic peaks from 3.68 ppm to 4.63 ppm and 3.08 ppm belonged to the -CH$_3$ group (2H, -CH$_3$O-) in the side chain and -CH$_2$ [26] in the main chain, respectively. In addition, the characteristic peaks of -CH$_2$ and -CH$_3$ groups in the polymer main chain were located at 0.89 ppm-2.01 ppm [27], and the characteristic absorption peaks of -CH$_2$ in the main chain appeared at 6.08 ppm [27]. In addition, as shown in the infrared spectrum (1c), the absorption peaks at 2942cm$^{-1}$ and 2868cm$^{-1}$ corresponded to the stretching vibration of the aliphatic group in the copolymer P (TFPMA-co-FAzo), respectively [28]. The C=O stretching vibration peak appeared at 1740cm$^{-1}$ [7]. The stretching vibration of -CH$_2$ on the benzene ring appeared at 1600 cm$^{-1}$. The telescopic vibration of the C-F key (569 and 745 cm$^{-1}$) appeared in the fingerprint area. The characteristic absorption peaks of C-O-C were at 1164 cm$^{-1}$ and 1241 cm$^{-1}$ [28]. Infrared analysis and $^1$H NMR characterization showed that P (TFPMA-co-FAzo) was successfully synthesized.

The THF solution of P (TFPMA-co-FAzo) was spin-coated on the glass substrate, and its UV-Vis absorption spectrum showed two peaks at 355 nm and 440 nm, corresponding to π-π* transitions and n-π* transitions [29] in the azobenzene derivative, respectively. When irradiated with ultraviolet light (λ = 365 nm), azobenzene produces a π-π* transition [10], which causes the absorption band at 355 nm to shift significantly to 320 nm and the intensity to decrease significantly, while the absorbance at 440 nm increases significantly, indicating that the azobenzene in the copolymer is converted from the trans isomer to the cis isomer [9] (figure 1d). The azobenzene cis isomer has a relatively large dipole moment (polarity) [10], which makes the azo-containing polymer film show stronger hydrophilicity. When exposed to visible light (λ = 450 nm), the azobenzene undergoes an n-π* transition [10], the absorption band at 320 nm undergoes a red-shift to 355 nm and the intensity rises significantly, while the absorption peak intensity decreases significantly at 440 nm, indicating that the azobenzene in the copolymer reversibly recovers from the cis isomer to the trans isomer [29] (figure 1e). Based on the reversible cis-trans isomerization cycle of the azophenyl group, the surface of the azo-containing polymer coating is endowed with excellent photosresponse and reversible wettability transition [9].

A PTFE-doped fluorinated azobenzene copolymer solution was spin-coated on a hydrophilic modified glass substrate to construct a composite blend film. Among them, the PTFE particles imparted a rough surface structure to the film surface, and the fluorine-containing azophenyl group in the copolymer imparted a wettable light-regulating property to the surface of the blended film. The
A blended membrane was able to achieve a reversible transition between hydrophilic (WCA = 20°) and hydrophobic (WCA = 105°) on the membrane surface under UV and Vis light irradiation (figure 2a). The effect of different copolymer solution concentrations on the water contact angle of the composite film surface is also studied (figure 2b). With the increase of the polymer solution concentration, the fluorine-containing group component on the surface of the prepared blend film increased, and the surface energy decreased. When the copolymer concentration was 5 wt%, the maximum surface contact angle of the composite film reached 105°. Besides, the water contact angle of the blended film prepared with a copolymer concentration ≥ 5 wt% can be reduced from 105° to about 45° under ultraviolet light, thereby achieving a hydrophobic to hydrophilic transition on the surface of the film; the wettability of the surface of the blended film can be reversibly restored from the hydrophilic (WCA = 45°) to the initial hydrophobic state (WCA = 105°).

Many studies have shown that the surface wettability of a material is determined by the chemical properties and surface roughness of the surface material [8]. Under constant copolymer solution concentration, as the doping ratio of PTFE powder continues to increase, the water contact angle on the membrane surface is significantly increased, and water contact angle on the surface of the blend film reaches maximum value of 105° when doped PTFE accounts for 10 wt% of the copolymer (figure 2c). The introduction of PTFE powder not only improves the roughness of the film surface, but also increases the content of fluorine-containing groups on the film surface, and reduces the surface energy of the film. It is worth noting that the PTFE doping improves the hydrophobic properties of the blended membrane, while increasing the stability of the blended membrane (figure 2d). The spin-coated film of the copolymer solution without PTFE is damaged to a certain degree only after 1 UV-Vis cycle, while the blended film doped with 10 wt% PTFE powder still shows good stability after 25 UV-Vis cycles (figure 2d).

Figure 1. Synthesis of (a) copolymer P (TFPMA-co-FAzo); (b) 1H NMR and (c) FTIR analysis of poly(TFPMA-co-FAzo) copolymer; UV-vis absorption spectrum of copolymer film with (d) UV light irradiation and (e) visible light irradiation.
In addition, the composition of the copolymer also has a large effect on the hydrophobicity and photosensitivity of the film surface (figures 2e and 2f). As the proportion of TFPMA in the copolymer gradually increases, the hydrophobicity of the composite film is improved, but the surface wettability and photoresponse are reduced to a certain extent. When TFPMA: FAzo = 50:50, the film surface has relatively high hydrophobicity and excellent photoresistance on film surface wettability, and the water contact angle remains stable at about 105°. Under UV light irradiation, the hydrophobicity of the polymer film (TFPMA: FAzo = 50:50) gradually decreases, and the minimum water contact angle (WCA = 45°) is reached after 40 s of irradiation (figure 2e); polymer film surface changes from hydrophobic to hydrophilic. When the film is further irradiated with Vis light, the water contact angle of the polymer film surface gradually increases with the irradiation time. When the irradiation time reaches 140 s, the film surface recovers its original hydrophobic properties (WCA = 105°) (figure 2f). The above results show that the surface wettability of the blended film has fast photoresponse and good performance stability.

In order to further understand the effect of the surface morphology and element distribution of the blend membrane on the light-regulated reversible wettability of the composite film, the surface morphology and surface element distribution of the blended film were characterized by SEM and EDS. As shown in figure 3, the surface of the blended membrane doped with PTFE has a greater surface
roughness than the surface without PTFE doping. With the continuous increase of the doping ratio, the surface roughness also improves significantly. When the doping ratio reaches about 10 wt%, the roughness reaches a maximum value; this is consistent with the finding that the static water contact angle on the surface of the blended film reaches maximum value (WCA = 105°) when doped with 10 wt% PTFE. As the doping ratio continued to increase, more severe agglomeration occurs on the film surface, resulting in no further improvement in the hydrophobicity. In this paper, a series of fluorine-containing photosensitive acrylate copolymers P (TFPMA-co-FAzo) were prepared by free radical solution polymerization. By increasing the content of the fluorinated acrylate monomer component in the copolymer, the hydrophobic properties of the surface of the polymer film were significantly improved, and the surface contact angle was increased from 40° to 90° (TFPMA: FAzo = 50: 50). Based on a simple hydrophobic particle doping strategy, the hydrophobic performance of the polymer film surface is further improved; when the content of micron-sized PTFE reaches 10 wt%, the surface of the blended film exhibits the highest hydrophobic performance with a static water contact angle of 115° and excellent surface wettability and light regulation performance. Under UV and Vis light irradiation, rapid and reversible conversion of the surface of the blended membrane from hydrophobic to hydrophilic can be achieved.

Figure 3. SEM image of the surface of the blend membrane with different PTFE doping concentrations.

4. Conclusion
In this paper, a series of fluorine-containing photosensitive acrylate copolymers P (TFPMA-co-FAzo) were prepared by free radical solution polymerization. By increasing the content of the fluorinated acrylate monomer component in the copolymer, the hydrophobic properties of the surface of the polymer film were significantly improved, and the surface contact angle was increased from 40° to 90° (TFPMA: FAzo = 50: 50). Based on a simple hydrophobic particle doping strategy, the hydrophobic performance of the polymer film surface is further improved; when the content of micron-sized PTFE
reaches 10 wt%, the surface of the blended film exhibits the highest hydrophobic performance with a static water contact angle of 115° and excellent surface wettability and light regulation performance. Under UV and Vis light irradiation, rapid and reversible conversion of the surface of the blended membrane from hydrophobic to hydrophilic can be achieved.

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