

Preparation and Characterization of UV-absorbing PVDF Membranes via Pre-irradiation Induced Graft Polymerization

Li Dong^{a,b}, Xiang-Dong Liu^a, Zheng-Rong Xiong^a, De-Kun Sheng^{a*}, Yan Zhou^{a,b}, and Yu-Ming Yang^{a*}

^a Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

^b University of Science and Technology of China, Hefei 230026, China

Abstract Herein, excellent UV-absorbing poly(vinylidene fluoride) (PVDF) membranes were fabricated through the pre-irradiation induced graft polymerization method. The PVDF chains irradiated with ^{60}Co γ -ray were modified with the polymerizable UV absorber 2-[2-hydroxy-5-[2-(methacryloyloxy)ethyl]phenyl]-2H-benzotriazole (RUVA-93). The influences of irradiation dose and monomer concentration on the prepared PVDF-g-PRUVA-93 membranes were investigated, and the optimal condition was eventually obtained. The chemical structures of the films were studied by ^1H -NMR, FTIR, and XRD. UV light transmittance and DSC tests were used to characterize the UV-absorbing performance and thermal property of the PVDF films before and after modification. The results proved that the PRUVA-93 side chains were successfully incorporated into the PVDF main chains and the obtained PVDF-g-PRUVA-93 films possessed remarkable UV-absorbing property. The modified membrane made under the optimized experiment condition could completely block the UV light in the range of 200–387 nm. Additionally, the transmittance of the PVDF-g-PRUVA-93 film could be reduced to 0.04% in 280–320 nm, where the light irradiation could damage polymer materials most seriously.

Keywords PVDF membrane; Modification; Irradiation; Grafting; UV-absorbing

Citation: Dong, L.; Liu, X. D.; Xiong, Z. R.; Sheng, D. K.; Zhou, Y.; Yang, Y. M. Preparation and characterization of UV-absorbing PVDF membranes via pre-irradiation induced graft polymerization. *Chinese J. Polym. Sci.* 2019, 37, 493–499.

INTRODUCTION

During the past decades, poly(vinylidene fluoride) (PVDF) has become one of the popular materials due to its excellent chemical and aging resistance, good thermal stability and mechanical properties, outstanding anti-oxidation performance, as well as many other merits.^[1–3] It has extensive applications in water and wastewater treatment,^[4] gas absorption, and membrane distillation.^[5,6] Many efforts have already been made to improve the anti-fouling property,^[7,8] hydrophilicity,^[9] hydrophobicity, and other new functions of PVDF.^[10–12] Methods including plasma treatment,^[11] physical blending,^[7,9] chemical treatment, and graft copolymerization are commonly used for PVDF modifications.^[13,14] The grafting polymerization can be achieved through various ways such as ozone pretreatment,^[15] UV light irradiation,^[3] ^{60}Co radiation,^[16] plasma-based processing technology as well as radical polymerization.^[17–19]

As aforementioned, lots of attempts have been made to modify PVDF. Nevertheless, there are very few researches on fabricating the UV-shielding PVDF film.^[20] As is known to all, discoloration, photo-destruction, and loss of mechanical properties of polymers can be caused by long time solar

ultraviolet (UV) radiation, particularly UV-B radiation.^[21,22] Therefore, when PVDF film is applied in the multilayer membranes, the modified one with outstanding UV-proofing property can protect the underlying materials from being destroyed. During the past years, a series of UV absorbers and fabricating methods have been investigated.^[23–27] The major classes of UV protection substances are traditional organic UV absorbers and inorganic metal oxide nanoparticles. The inorganic shielding substances such as TiO_2 ,^[28] ZnO ,^[29] SiO_2 , and CeO can reflect and scatter the UV radiation.^[30,31] The organic UV absorbers, for example, benzophenones, benzotriazoles, cinnamates in addition to triazines, can transform the radiation energy into less damaging thermal energy through the deactivation process.^[32–35] Besides, some novel UV-proof products have also been found, including polydopamine (PDA),^[36] graphene oxide (GO),^[37] Fe^{3+} doped Mg/Al layered double hydroxides ($\text{Mg/Al} + \text{Fe LDHs}$),^[38] carbon quantum dots (CQDs),^[39] sepia eumelanin (SE),^[40] mycosporines,^[41] mycosporine-like amino acids (MAAs),^[42] and other natural UV-protectants.^[43]

Benzotriazoles, as one of the most important families of organic compounds, have been widely applied in a variety of plastic products.^[44] The benzotriazole UV absorbers can be incorporated into PVDF to make UV-shielding membranes. Unfortunately, small molecule UV absorbers tend to migrate from the polymer matrix during the service life of the polymer materials. To make a strong combination between the

* Corresponding authors: E-mail dksheng@ciac.ac.cn (D.K.S.)

E-mail ymyang@ciac.ac.cn (Y.M.Y.)

Received August 31, 2018; Accepted October 19, 2018; Published online November 14, 2018

UV absorbers and polymer matrix, grafting technology can be used. Among the varied methods that have been reported, radiation-induced graft polymerization is a good approach for modifying polymers because of its non-selectivity, mild reaction temperature, strong penetration ability, and ease of operation performances.^[45,46]

In this study, the small molecule UV absorber, 2-[2-hydroxy-5-[2-(methacryloyloxy)ethyl]phenyl]-2*H*-benzotriazole (RUVA-93), was grafted onto PVDF powders by the pre-irradiation induced graft copolymerization. An optimal experiment condition was finally obtained after the influences of irradiation dose and monomer amounts were investigated in detail. The excellent UV-absorbing property of as-prepared PVDF-*g*-PRUVA-93 films was assessed by measuring the UV transmittance with a UV-Vis spectrometer. Besides, the chemical compositions and thermal properties of the modified membranes were also determined.

EXPERIMENTAL

Materials

Poly(vinylidene fluoride) (PVDF) powders (Solef® 6010) were provided by Solvay Co., Ltd. 2-[2-Hydroxy-5-[2-(methacryloyloxy)ethyl]phenyl]-2*H*-benzotriazole (RUVA-93, > 98.0%) was obtained from Tokyo Chemical Industry Co., Ltd. Dimethylacetamide (DMAc), ethanol, and butanol were AR grade and purchased from Beijing Chemical Works. Methylene blue and titanium oxide (TiO₂, 99.8%, 40 nm) were supplied by Aladdin Chemistry Co., Ltd. PVDF powders were washed with deionized water to remove impurities, and dried in vacuum until a constant weight was obtained. All other mentioned chemicals were used without further purification.

Pre-irradiation Induced Graft Polymerization

The UV-absorbing PVDF-*g*-PRUVA-93 copolymer was made according to the process shown in Fig. 1. The purified PVDF powders were irradiated with a 15 kGy dose in air using γ -ray from a ⁶⁰Co source at room temperature. After irradiation, the powders were stored at -20 °C in a refrigerator before use. Then 5.88 g of irradiated PVDF powders and 1.12 g of RUVA-93 (the concentration of RUVA-93 was 16 wt%) were added into the twin screw compounder (Micro 15cc Twin Screw Compounder, DSM Xplore, Geleen, Netherlands) for 6 min at 190 °C with the rotor speed of 50 r·min⁻¹ to initiate the copolymerization. The obtained copolymer was dissolved in DMAc, and then precipitated with ethanol. After that, the copolymer was

washed by Soxhlet extraction with butanol for 24 h to remove the residual monomers completely. The PVDF-*g*-PRUVA-93 copolymer was finally obtained after being completely dried.

Preparation of PVDF Membranes

The neat and modified PVDF films were made *via* the solution casting method. PVDF powders (0.5 g) were added into a flask with 10 mL of DMAc. The mixture was stirred for 3 h at 50 °C. The homogeneous solution was then cast onto a horizontal plate in an oven and spread with the casting blade. The temperature of the oven was kept at 65 °C. After the solvent was carefully evaporated for 40 min, the temperature was turned up to 200 °C in order to remove the residual DMAc. The neat PVDF film with the thickness of 40 μ m was finally obtained after the film was cooled down to 23 °C. The manufacturing process of PVDF-*g*-PRUVA-93 membrane was the same as that of PVDF film.

UV-shielding Performance of the Films

The degradation of methylene blue solution under UV radiation was further used to assess the UV-proofing property of the obtained PVDF-*g*-PRUVA-93 film. Methylene blue solution (20 mL, 1.76×10^{-5} mol·L⁻¹) and TiO₂ (10 mg) were added into a transparent glass vial. The obtained solution was stirred in dark for 30 min to assure sufficient dispersion. The neat and modified PVDF membranes were used to cover the vial during UV irradiation (45 W), respectively. The distance between the films and the lamp was 8 cm, and the irradiation was conducted at temperature of 20 °C under constant stirring. The methylene blue solution (0.7 mL) was hourly taken out of the vial, followed by filtration of TiO₂. The absorbance of the initial and irradiated solution was then measured by a UV-Vis spectrophotometer. The remarkable UV-blocking property of the modified membrane was proved by the value change of I ($I = A_t/A_0 \times 100\%$). In the formula, A_0 and A_t were the absorbance of methylene blue solution before and after the UV radiation, respectively. In addition, to make a clearer contrast, photographs of the methylene blue solutions irradiated for different time were taken as well.

Material Characterization

¹H-NMR spectrum of the modified PVDF was recorded on a Bruker AV 400 instrument at room temperature. FTIR spectra were recorded using a Fourier transform infrared spectrometer (Bruker Vertex 70, Germany) in the wave-number region of 4000–600 cm⁻¹. The spectra were collected at ambient temperature with a resolution of 2 cm⁻¹. Ion chro-

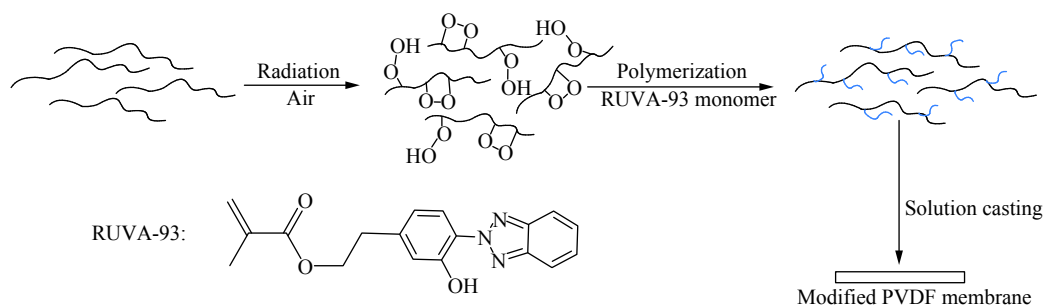


Fig. 1 Schematic illustration for the PVDF-*g*-PRUVA-93 membrane preparation

matography (Dionex ICS-1000, USA) was used to determine the content of fluorine element in graft copolymer. The optical performance of samples from 200 nm to 800 nm was investigated by the UV-Vis spectrophotometer (Shimadzu UV 3600, Japan). The crystallographic structures of PVDF film before and after modification were analyzed by an X-ray diffractometer (Bruker D8 Advance, Germany) with Cu K α radiation ($\lambda = 0.154$ nm). The thermal properties of the films were studied by a differential scanning calorimeter (DSC, TA Q20, USA) at a heating rate of 10 °C·min⁻¹ in the temperature range of 30–250 °C under a dry N₂ atmosphere. UV-shielding performance tests were conducted in an aging testing chamber (GT-7035-UB, China).

RESULTS AND DISCUSSION

As is known to us, free radicals can be generated in polymer chains *via* radiation. Hydroxyl and per-oxy groups can be obtained after the irradiated polymer is oxidized by oxygen in air. Then the per-oxy groups can produce free radicals to initiate copolymerization of the monomers. Therefore, many free radicals could be generated in PVDF chains after the powers were irradiated with ⁶⁰Co γ -ray source and the thermal initiated graft of RUVA-93 was then conducted in a twin screw compounder. The successful copolymerization was proved by the structure and UV-absorbing property characterizations as shown below.

Chemical Structure of PVDF-g-PRUVA-93

Fig. 2 shows the ¹H-NMR spectrum of the prepared PVDF-g-PRUVA-93. The resonance signal at around 2.92 ppm is ascribed to the tail-to-head structure of PVDF main chains, whereas the signal at 2.25 ppm is assigned to the tail-to-tail bonding arrangement. The spectrum shows no signals at around 6.12 and 5.73 ppm, indicating that there are no residual RUVA-93 molecules. In addition, some new signals corresponding to the protons of PRUVA-93 appear in the spectrum. The signal at around 10.52 ppm is responsible for the proton of phenolic hydroxyl (H₈). The signals observed at about 7.20, 6.95–6.77, and 7.62 ppm are assigned to the aromatic protons H₁ and H₂, H₃–H₆, and H₇, respectively.

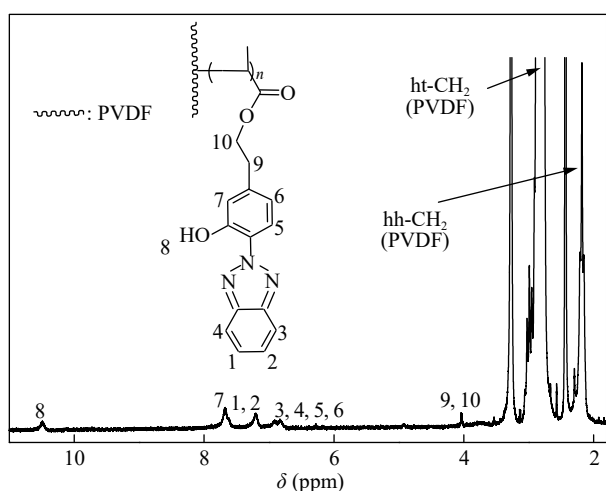


Fig. 2 ¹H-NMR spectrum of PVDF-g-PRUVA-93

The chemical shift at 4.04 ppm is ascribed to H₉ and H₁₀.

FTIR spectra of RUVA-93 and PVDF films before and after functionalization are presented in Fig. 3. In the spectrum of RUVA-93, the characteristic absorption bands at 3384 and 1728 cm⁻¹ are ascribed to the stretching vibrations of the alcoholic hydroxyl and ester carbonyl groups, respectively. The bands at wavenumbers of 1539 and 1397 cm⁻¹ are assigned to C=C of benzene ring and C=N stretching vibration. Notably, the new distinctive bands at about 1733, 1514, and 1387 cm⁻¹ which are in accordance with the characteristic bands of RUVA-93 appear in the spectrum of PVDF-g-PRUVA-93 membrane in comparison to that of the neat PVDF film. These results clearly prove that PVDF was successfully modified *via* the radiation-induced grafting with reactive UV absorber RUVA-93.

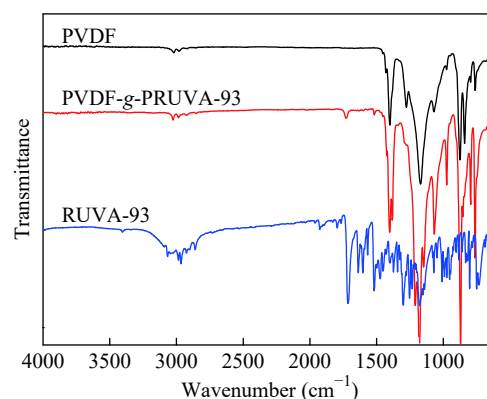


Fig. 3 FTIR spectra of RUVA-93, the neat PVDF, and the obtained PVDF-g-PRUVA-93 film

Influence of Grafting Condition

During the experiment process, it was found that the radiation dose and monomer concentration could greatly affect the performance of the obtained PVDF-g-PRUVA-93 films. Hence, to detailedly evaluate the influence of grafting parameters, the graft copolymerization with different radiation doses and RUVA-93 concentrations was further conducted. To characterize the PVDF-g-PRUVA-93 membranes, FTIR and UV-Vis transmittance tests were applied.

Influence of radiation dose

As active sites can be generated in the irradiated PVDF chains, more free radicals may be produced at higher absorbed doses. To confirm the effect of radiation dose, PVDF powers irradiated with 5, 10, 20, and 25 kGy were made, respectively. Other copolymerization conditions and the film preparation process were the same as above.

The UV-Vis transmittance spectra and transmittance change tendency curve of the PVDF-g-PRUVA-93 membranes made under different pre-radiation doses are shown in Figs. 4 and 5, respectively. As shown in Fig. 4, it is evident that the neat PVDF film is nearly transparent across the whole range, whereas there is an obvious transmittance decrease throughout the wavelength region of 200–400 nm after PRUVA-93 chains were incorporated. The transmittance decreases and the UV absorbing ranges extend gradually with the increasing radiation dose as more UV absorbers are grafted onto the PVDF chains. When the irradi-

ation dose is 5 kGy, the transmittance of PVDF-g-PRUVA-93 film between 200 and 325 nm is less than 58.7%; however, when the irradiation dose increases to 25 kGy, the transmittance is below 15% in the range of 200–350 nm. Fig. 5 illustrates the change tendency of film transmittance. As noticed in the figure, there are significant transmittance changes (at 300 nm) for the films. For the PVDF film made without pre-irradiation, the transmittance is 95.37% at the wavelength of 300 nm. Clearly, there is a substantial transmittance decrease along with the dose increase from 5 kGy to 25 kGy. The transmittance of PVDF-g-PRUVA-93 films made with radiation of 20 and 25 kGy are 10.64% and 6.46%, respectively. The reason is that more reactive sites appear in the modified PVDF chains with the increasing radiation dose, which is in favor of the copolymerization. Hence, it can be concluded that radiation dose plays an important role in the pre-irradiation induced graft polymerization. More active sites can be generated in the polymer chains with the higher radiation dose. Additionally, the radiation dose of 25 kGy was used in the following contrast experiment, because the decrease rate of film transmittance becomes slower when the dose is larger than 20 kGy.

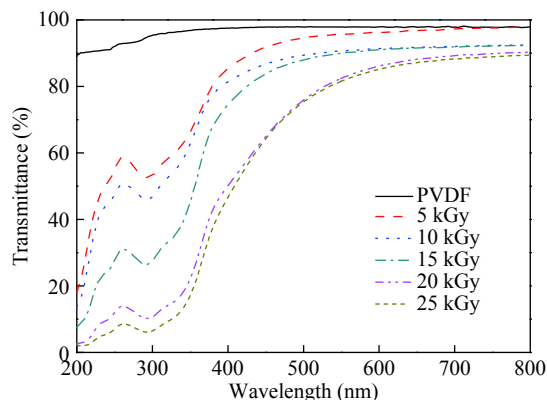


Fig. 4 UV-Vis transmittance spectra of the neat PVDF film and PVDF-g-PRUVA-93 films made under different irradiation doses

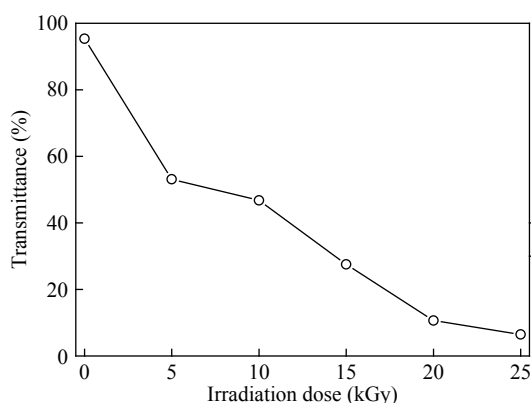


Fig. 5 Transmittance tendency of the PVDF-g-PRUVA-93 membranes at the wavelength of 300 nm

Influence of RUVA-93 concentration

To verify the feed concentration of RUVA-93 on the structure and property of modified PVDF films, copolymerization was conducted at the RUVA-93 concentrations of 4 wt%,

8 wt%, 12 wt%, and 16 wt%. The radiation dose was 25 kGy and other conditions and operations were the same as above.

FTIR spectra of the original PVDF and PVDF-g-PRUVA-93 films were recorded to study the influence of RUVA-93 concentration on film structure, and the results are given in Fig. 6. Obviously, in the spectrum of PVDF film without any treatment, there is no band in the region of 1500–2000 cm^{-1} . However, for the spectra of PVDF-g-PRUVA-93, the band at around 1730 cm^{-1} , which is ascribed to the ester carbonyl stretching vibration, can be clearly observed. And the band intensity increases at the higher monomer concentrations. Besides, another new band at 1513 cm^{-1} which is assigned to C=C bonds of benzene rings also appears when the monomer concentration is 12 wt%. The new bands are all in accordance with those of RUVA-93. These results clearly indicate the successful graft of PRUVA-93 to the PVDF backbones, and more side chains are incorporated with increasing monomer concentration. Thus, the concentration of RUVA-93 has an important influence on the structure of PVDF-g-PRUVA-93 films.

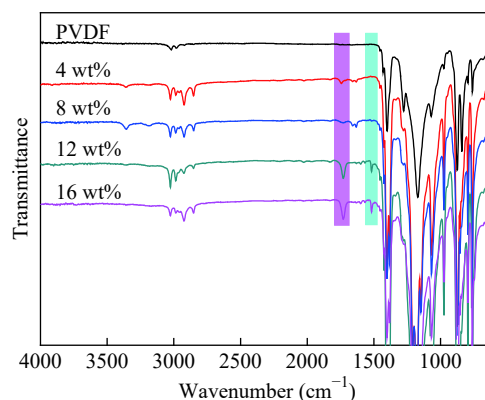


Fig. 6 FTIR spectra of the neat PVDF membrane and PVDF-g-PRUVA-93 films made with different monomer concentrations

Fig. 7 shows the transmittance variation (at 300 nm) of the neat and modified PVDF films obtained with different RUVA-93 concentrations. For the original PVDF film, the transmittance of 95.37% means almost no UV absorbance. After modified with 4 wt% of RUVA-93, the transmittance of obtained film quickly drops to 6.46%. With the concentration continuously increasing, the transmittance reduces to as low as 0.08%. Nevertheless, when the concentration increases to 16 wt%, the transmittance change is not so obvious.

The UV-Vis transmittance spectra of the modified PVDF films measured within 200–800 nm are presented in Fig. 8. As can be seen, there is a considerable absorbance in the UV region when films are modified with RUVA-93 compared with the original PVDF film that almost has no absorbance across the whole range. It means that the modified PVDF films have fairly good UV-absorbing property. When the monomer concentration is 8 wt%, the light transmittance of PVDF-g-PRUVA-93 membrane in the region from 200 nm to 357 nm can decrease to less than 6.82%. When 12 wt% of RUVA-93 is conducted, the light transmittance between 200 and 377 nm is less than 0.86%. Clearly, the UV absorbing range becomes wider at higher RUVA-93 concentration. In

addition, through analysis and comparison of the spectra, the film modified with 16 wt% of RUVA-93 shows the best UV-shielding property. The PVDF-g-PRUVA-93 membrane can completely block the UV light in the range of 200–387 nm as the transmittance is below 1%. Besides, the light between 280 and 320 nm can lead to the most serious damage to materials, and the transmittance of the PVDF-g-PRUVA-93 film at that region reduces to below 0.04%.

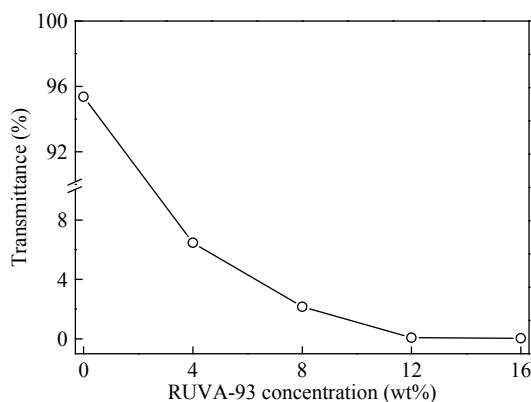


Fig. 7 Transmittance tendency of the PVDF-g-PRUVA-93 films made with different monomer concentrations at the wavelength of 300 nm

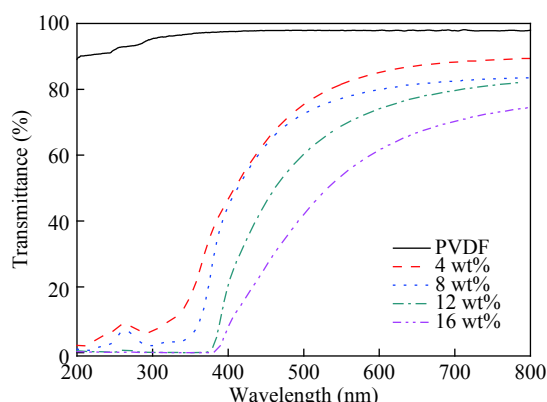


Fig. 8 UV-Vis transmittance spectra of the neat PVDF and PVDF-g-PRUVA-93 films made with different monomer concentrations

Concluding the discussions above, it is reasonable to state that the irradiation dose and RUVA-93 concentration have very important influences on both UV-blocking property and chemical structures of the fabricated PVDF-g-PRUVA-93 films. Based on the series of comparisons above, the best experiment conditions are obtained. The PVDF-g-PRUVA-93 film made with 25 kGy irradiation and 16 wt% of RUVA-93 demonstrates fabulous UV-absorbing property. The UV-shielding performance, thermal property, grafting degree, as well as the structure of PVDF-g-PRUVA-93 film fabricated under the optimum condition were further investigated.

Degree of Grafting

The degree of grafting (DG) of the PVDF-g-PRUVA-93 copolymer made under optimal condition was determined by fluorine elemental analysis. The reason is that the mass increase measurement is inaccurate due to the inevitable mass loss during experiment process. In this work, DG was

calculated according to the following formula:

$$DG = (19 - 32W_F)/32W_F \quad (1)$$

where W_F is the mass fraction of fluorine element. The element measurement shows that W_F of the modified PVDF is 52.53%, lower than that of the original PVDF (61.29%) as there is no fluorine in the PRUVA-93 segments. It can be calculated that the DG of PVDF-g-PRUVA-93 is 13.41%.

UV-shielding Performance of Films

Degradation of methylene blue solution was studied here to further examine the UV-shielding performance of PVDF-g-PRUVA-93 membrane prepared under the optimal conditions. As shown in Fig. 9, there is an obvious drop on the photodegradation curve of the neat PVDF film protected methylene blue solution after being irradiated with the UV light. The absorption intensity of methylene blue shows a decrease of 74.9% with the irritation time increasing to 6 h. However, for the solution protected with PVDF-g-PRUVA-93 membrane, the absorption change is relatively slight. The degraded content of methylene blue is only about 12.37%. Furthermore, by comparing the inset photos, it can be learned that there is a very obvious color change in the neat PVDF-protected methylene blue solution with increasing irritation time. The color of the solution covered by neat PVDF film is very light after being irradiated for 6 h, while the solution protected with the modified PVDF film is still dark blue. Altogether, the test results demonstrate that PVDF-g-PRUVA-93 film made under optimal condition has superb UV-shielding property, which thereby makes it a good surface UV-protecting material.

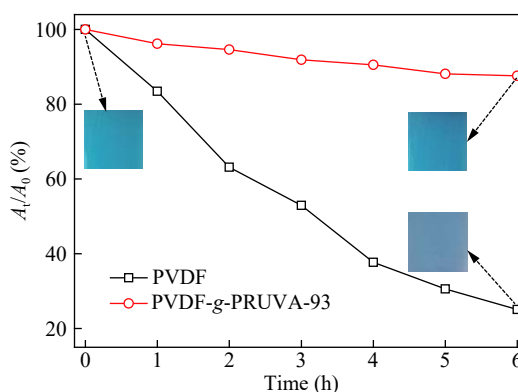


Fig. 9 The photodegradation curves of methylene blue solution covered with the neat PVDF and PVDF-g-PRUVA-93 membrane (optimal) (Inset: photos of the methylene blue solution before and after irradiation.)

XRD Analysis

XRD patterns of the neat and modified PVDF films are presented in Fig. 10. The XRD pattern of the neat PVDF film exhibits (100), (020), (110), and (111) typical lattice planes at 17.7°, 18.4°, 20.1°, and 26.6°, which proves the PVDF used here is in α -crystal form. After grafting, there are no changes in the sites of peaks, whereas the intensities become weak. Thus, the crystal form of PVDF film after the grafting copolymerization process does not change, while the crystallinity degree of the PVDF-g-PRUVA-93 film becomes lower compared to that of the neat PVDF film.

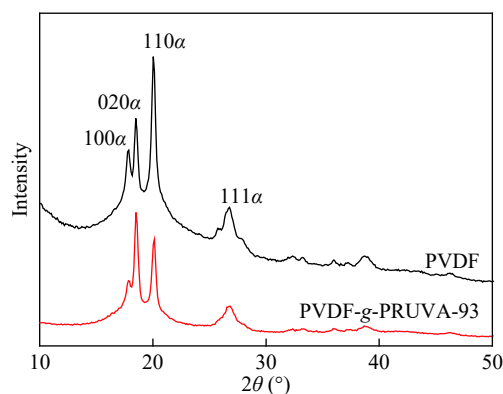


Fig. 10 XRD patterns of the PVDF and PVDF-g-PRUVA-93 films

DSC Analysis

Phase transformation of neat PVDF and the obtained PVDF-g-PRUVA-93 membranes was evaluated by DSC and the curves are displayed in Fig. 11. Obviously, the melting temperature (T_m) of the untreated PVDF film is about 171.56 °C. After grafting, it decreases to 170.66 °C due to the presence of PRUVA-93 chains. Besides, the melting enthalpy (ΔH_m) of PVDF-g-PRUVA-93 film is 60.13 J·g⁻¹, lower than that of neat PVDF film (66.32 J·g⁻¹). The crystallinity degrees of the original PVDF and PVDF-g-PRUVA-93 films calculated based on reference data are 63.40% and 57.48%, respectively.^[8] This is remarkably consistent with the test results of XRD. Hence, the DSC results further illustrate the successful grafting of PRUVA-93 onto PVDF main chains *via* the pre-irradiation induced polymerization method.

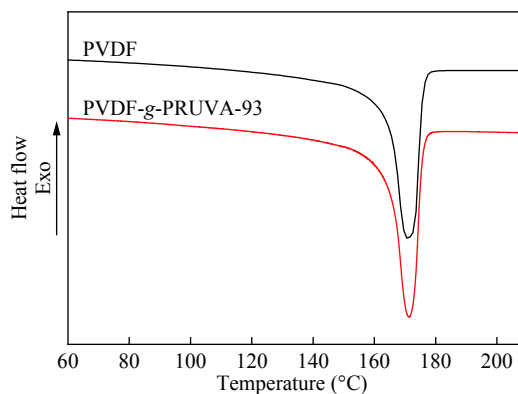


Fig. 11 DSC curves of the neat PVDF and PVDF-g-PRUVA-93 membranes

CONCLUSIONS

The functional PVDF membrane that has superb UV-absorbing property was successfully made by pre-irradiation induced grafting of reactive UV absorber RUVA-93 onto the PVDF backbones. The existence of PRUVA-93 chains was determined by FTIR, ¹H-NMR, XRD as well as DSC measurements. Besides, after plenty of experimental comparisons, we proved that the absorbed dose and monomer concentration were inextricably relevant to the chemical structure and UV-proofing performance of the functionalized PVDF films. The PVDF-g-PRUVA-93 membrane produced

under the optimal condition could completely block the UV light within 200–387 nm. Furthermore, the light transmittance of the functional film at wavelength of 280–320 nm, which can cause the most serious damage to the polymer materials, could reduce to as low as 0.04%. The UV-shielding performance of the PVDF-g-PRUVA-93 film was further testified by the measurement of methylene blue photo-degradation. Thus, the pre-irradiation induced graft polymerization approach for preparing the UV-absorbing PVDF membranes shown in this study is very efficient and has bright application prospects.

REFERENCES

- Kang, G. D.; Cao, Y. M. Application and modification of poly(vinylidene fluoride) (PVDF) membranes—A review. *J. Membr. Sci.* **2014**, *463*, 145–165.
- Otitoju, T. A.; Ahmad, A. L.; Ooi, B. S. Polyvinylidene fluoride (PVDF) membrane for oil rejection from oily wastewater: A performance review. *J. Water. Process. Eng.* **2016**, *14*, 41–59.
- Rahimpour, A.; Madaeni, S. S.; Zereshti, S.; Mansourpanah, Y. Preparation and characterization of modified nano-porous PVDF membrane with high antifouling property using UV photo-grafting. *Appl. Surf. Sci.* **2009**, *255*, 7455–7461.
- Zuo, J. H.; Cheng, P.; Chen, X. F.; Yan, X.; Guo, Y. J.; Lang, W. Z. Ultrahigh flux of polydopamine-coated PVDF membranes quenched in air *via* thermally induced phase separation for oil/water emulsion separation. *Sep. Purif. Technol.* **2018**, *192*, 348–359.
- Wu, X. N.; Zhao, B.; Wang, L.; Zhang, Z. H.; Zhang, H. W.; Zhao, X. H.; Guo, X. F. Hydrophobic PVDF/graphene hybrid membrane for CO₂ absorption in membrane contactor. *J. Membr. Sci.* **2016**, *520*, 120–129.
- Ji, J.; Liu, F.; Awanis Hashim, N.; Moghareh Abed, M. R.; Li, K. Poly(vinylidene fluoride) (PVDF) membranes for fluid separation. *Reac. Funct. Polym.* **2015**, *86*, 134–153.
- Zhao, C. Q.; Xu, X. C.; Chen, J.; Yang, F. L. Effect of graphene oxide concentration on the morphologies and antifouling properties of PVDF ultrafiltration membranes. *J. Environ. Chem. Eng.* **2013**, *1*, 349–354.
- Chen, L. F.; Hou, Z. C.; Lu, X. F.; Chen, P.; Liu, Z. Y.; Shen, L. G.; Bian, X. K.; Qin, Q. Antifouling microfiltration membranes prepared from poly(vinylidene fluoride)-graft-poly(*N*-vinyl pyrrolidone) powders synthesized *via* pre-irradiation induced graft polymerization. *J. Appl. Polym. Sci.* **2013**, *128*, 3949–3956.
- Zhu, Z. Y.; Jiang, J. L.; Wang, X. D.; Huo, X. N.; Xu, Y. W.; Li, Q. Q.; Wang, L. Improving the hydrophilic and antifouling properties of polyvinylidene fluoride membrane by incorporation of novel nanohybrid GO@SiO₂ particles. *Chem. Eng. J.* **2017**, *314*, 266–276.
- Wu, C. R.; Tang, W. Y.; Zhang, J. H.; Liu, S. H.; Wang, Z. Y.; Wang, X.; Lu, X. L. Preparation of super-hydrophobic PVDF membrane for MD purpose *via* hydroxyl induced crystallization-phase inversion. *J. Membr. Sci.* **2017**, *543*, 288–300.
- Yang, C.; Li, X. M.; Gilron, J.; Kong, D. F.; Yin, Y.; Oren, Y.; Linder, C.; He, T. CF₄ plasma-modified superhydrophobic PVDF membranes for direct contact membrane distillation. *J. Membr. Sci.* **2014**, *456*, 155–161.
- Chen, X.; He, Y.; Shi, C. C.; Fu, W. G.; Bi, S. Y.; Wang, Z. Y.; Chen, L. Temperature- and pH-responsive membranes based on poly(vinylidene fluoride) functionalized with microgels. *J. Membr. Sci.* **2014**, *469*, 447–457.
- Sun, C. G.; Feng, X. S. Enhancing the performance of PVDF membranes by hydrophilic surface modification *via* amine treatment. *Sep. Purif. Technol.* **2017**, *185*, 94–102.
- Cai, T.; Neoh, K. G.; Kang, E. T. Surface-functionalized and

- surface-functionalizable poly(vinylidene fluoride) graft copolymer membranes *via* click chemistry and atom transfer radical polymerization. *Langmuir* **2011**, *27*, 2936–2945.
- 15 Xu, L. Q.; Chen, J. C.; Wang, R.; Neoh, K. G.; Kang, E. T.; Fu, G. D. A poly(vinylidene fluoride)-graft-poly(dopamine acrylamide) copolymer for surface functionalizable membranes. *RSC Adv.* **2013**, *3*, 25204–25214.
 - 16 Xu, C. Q.; Huang, W.; Zhou, Y. F.; Yan, D. Y.; Chen, S. T.; Huang, H. Graft copolymerization of *N*-vinyl-2-pyrrolidone onto pre-irradiated poly(vinylidene fluoride) powder. *Radiat. Phys. Chem.* **2012**, *81*, 426–431.
 - 17 Zhao, X. Z.; Xuan, H. X.; Qin, A. W.; Liu, D. P.; He, C. J. Improved antifouling property of PVDF ultrafiltration membrane with plasma treated PVDF powder. *RSC Adv.* **2015**, *5*, 64526–64533.
 - 18 Liu, J.; Shen, X.; Zhao, Y. P.; Chen, L. Acryloylmorpholine-grafted PVDF membrane with improved protein fouling resistance. *Ind. Eng. Chem. Res.* **2013**, *52*, 18392–18400.
 - 19 Dong, L.; Liu, X. D.; Xiong, Z. R.; Sheng, D. K.; Zhou, Y.; Lin, C. H.; Yang, Y. M. Design of UV-absorbing PVDF membrane *via* surface-initiated AGET ATRP. *Appl. Surf. Sci.* **2018**, *435*, 680–686.
 - 20 Dong, L.; Liu, X. D.; Xiong, Z. R.; Sheng, D. K.; Lin, C. H.; Zhou, Y.; Yang, Y. M. Fabrication of highly efficient ultraviolet absorbing PVDF membranes *via* surface polydopamine deposition. *J. Appl. Polym. Sci.* **2018**, *135*, 45746.
 - 21 Wang, G. R.; Xu, S. M.; Xia, C. H.; Yan, D. P.; Lin, Y. J.; Wei, M. Fabrication of host-guest UV-blocking materials by intercalation of fluorescent anions into layered double hydroxides. *RSC Adv.* **2015**, *5*, 23708–23714.
 - 22 Cohen, S.; Haham, H.; Pellach, M.; Margel, S. Design of UV-absorbing polypropylene films with polymeric benzotriazole based nano- and microparticle coatings. *ACS Appl. Mater. Interfaces* **2016**, *9*, 868–875.
 - 23 Hattori, H.; Ide, Y.; Sano, T. Microporous titanate nanofibers for highly efficient UV-protective transparent coating. *J. Mater. Chem. A* **2014**, *2*, 16381–16388.
 - 24 Kainulainen, T. P.; Sirviö, J. A.; Sethi, J.; Hukka, T. I.; Heiskanen, J. P. UV-blocking synthetic biopolymer from biomass-based bifuran diester and ethylene glycol. *Macromolecules* **2018**, *51*, 1822–1829.
 - 25 Lizundia, E.; Ruiz-Rubio, L.; Vilas, J. L.; León, L. M. Poly(L-lactide)/ZnO nanocomposites as efficient UV-shielding coatings for packaging applications. *J. Appl. Polym. Sci.* **2016**, *133*, 42426.
 - 26 Feng, Y.; Zhang, J. M.; He, J. S.; Zhang, J. Transparent cellulose/polyhedral oligomeric silsesquioxane nanocomposites with enhanced UV-shielding properties. *Carbohydr. Polym.* **2016**, *147*, 171–177.
 - 27 Ge, F. J.; Ding, Y. Y.; Yang, L.; Huang, Y.; Jiang, L.; Dan, Y. Effect of the content and distribution of ultraviolet absorbing groups on the UV protection and degradation of polylactide films. *RSC Adv.* **2015**, *5*, 70473–70481.
 - 28 Du, J. Z.; Sun, H. Polymer/TiO₂ hybrid vesicles for excellent UV screening and effective encapsulation of antioxidant agents. *ACS Appl. Mater. Interfaces* **2014**, *6*, 13535–13541.
 - 29 Senatova, S. I.; Senatov, F. S.; Kuznetsov, D. V.; Stepashkin, A. A.; Issi, J. P. Effect of UV-radiation on structure and properties of PP nanocomposites. *J. Alloy. Compd.* **2017**, *707*, 304–309.
 - 30 Woo, H.; Char, K. Transparent organosilicate hybrid films with thermally insulating and UV-blocking properties based on silica/titania hybrid hollow colloidal shells. *Macromol. Res.* **2013**, *21*, 1004–1010.
 - 31 Aguirre, M.; Paulis, M.; Leiza, J. R. UV screening clear coats based on encapsulated CeO₂ hybrid latexes. *J. Mater. Chem. A* **2013**, *1*, 3155–3162.
 - 32 Zhao, Y.; Xu, Z. G.; Wang, X. G.; Lin, T. Superhydrophobic and UV-blocking cotton fabrics prepared by layer-by-layer assembly of organic UV absorber intercalated layered double hydroxides. *Appl. Surf. Sci.* **2013**, *286*, 364–370.
 - 33 Zhang, Y.; Han, J. R.; Wu, S. Y.; Qi, Z. G.; Xu, J.; Guo, B. H. Synthesis, physical properties and photodegradation of functional poly(butylene succinate) covalently linking UV stabilizing moieties in molecular chains. *Colloid. Surf. A* **2017**, *524*, 160–168.
 - 34 Lei, H. B.; He, D. L.; Guo, Y. N.; Tang, Y. N.; Huang, H. Q. Synthesis and characterization of UV-absorbing fluorine-silicone acrylic resin polymer. *Appl. Surf. Sci.* **2018**, *442*, 71–77.
 - 35 Dong, L.; Liu, X. D.; Xiong, Z. R.; Sheng, D. K.; Lin, C. H.; Zhou, Y.; Yang, Y. M. Preparation and characterization of functional poly(vinylidene fluoride) (PVDF) membranes with ultraviolet-absorbing property. *Appl. Surf. Sci.* **2018**, *444*, 497–504.
 - 36 Wang, Y.; Su, J.; Li, T.; Ma, P. M.; Bai, H. Y.; Xie, Y.; Chen, M. Q.; Dong, W. F. A novel UV-shielding and transparent polymer film: When bioinspired dopamine-melanin hollow nanoparticles join polymers. *ACS Appl. Mater. Interfaces* **2017**, *9*, 36281–36289.
 - 37 de Moraes, A. C. M.; Andrade, P. F.; de Faria, A. F.; Simões, M. B.; Salomão, F. C. C. S.; Barros, E. B.; Goncalves, M. C.; Alves, O. L. Fabrication of transparent and ultraviolet shielding composite films based on graphene oxide and cellulose acetate. *Carbohydr. Polym.* **2015**, *123*, 217–227.
 - 38 Wang, X. L.; Zhou, S. X.; Wu, L. M. Fabrication of Fe³⁺ doped Mg/Al layered double hydroxides and their application in UV light-shielding coatings. *J. Mater. Chem. C* **2014**, *2*, 5752–5758.
 - 39 Hess, S. C.; Permatasari, F. A.; Fukazawa, H.; Schneider, E. M.; Balgis, R.; Ogi, T.; Okuyama, K.; Stark, W. J. Direct synthesis of carbon quantum dots in aqueous polymer solution: One-pot reaction and preparation of transparent UV-blocking films. *J. Mater. Chem. A* **2017**, *5*, 5187–5194.
 - 40 Wang, Y.; Li, T.; Ma, P. M.; Bai, H. Y.; Xie, Y.; Chen, M. Q.; Dong, W. F. Simultaneous enhancements of UV-shielding properties and photostability of poly(vinyl alcohol) *via* incorporation of sepia eumelanin. *ACS Sustain. Chem. Eng.* **2016**, *4*, 2252–2258.
 - 41 Fernandes, S. C. M.; Alonso-Varona, A.; Palomares, T.; Zubilaga, V.; Labidi, J.; Bulone, V. Exploiting mycosporines as natural molecular sunscreens for the fabrication of UV-absorbing green materials. *ACS Appl. Mater. Interfaces* **2015**, *7*, 16558–16564.
 - 42 Rastogi, R. P.; Incharoensakdi, A. Analysis of UV-absorbing photoprotectant mycosporine-like amino acid (MAA) in the cyanobacterium *Arthrospira* sp. CU2556. *Photochem. Photobiol. Sci.* **2014**, *13*, 1016–1024.
 - 43 Nguyen, K. H.; Chollet-Krugler, M.; Gouault, N.; Tomasi, S. UV-protectant metabolites from lichens and their symbiotic partners. *Nat. Prod. Rep.* **2013**, *30*, 1490–1508.
 - 44 Cohen, S.; Kolitz-Domb, M.; Haham, H.; Gelber, C.; Margel, S. Engineering of UV-absorbing polypropylene films containing poly(2-(2'-hydroxy-5'-methacryloxyethylphenyl)-2H-benzotriazole) nanoparticles. *Polym. Adv. Technol.* **2017**, *28*, 897–904.
 - 45 Qin, Q.; Hou, Z. C.; Lu, X. F.; Bian, X. K.; Chen, L. F.; Shen, L. G.; Wang, S. Microfiltration membranes prepared from poly(*N*-vinyl-2-pyrrolidone) grafted poly(vinylidene fluoride) synthesized by simultaneous irradiation. *J. Membr. Sci.* **2013**, *427*, 303–310.
 - 46 Shin, I. H.; Hong, S.; Lim, S. J.; Son, Y. S.; Kim, T. H. Surface modification of PVDF membrane by radiation-induced graft polymerization for novel membrane bioreactor. *J. Ind. Eng. Chem.* **2017**, *46*, 103–110.