

Preirradiation-Induced Emulsion Graft Polymerization of Glycidyl Methacrylate onto Poly(vinylidene fluoride) Powder

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ABSTRACT: An epoxy-group-containing monomer, glycidyl methacrylate (GMA), was grafted onto poly(vinylidene fluoride) powder via preirradiation-induced emulsion graft polymerization. The existence of graft chains was proven by chemical structure characterization with Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy analysis. The degree of grafting was calculated by means of fluorine content analysis. A kinetic study indicated that, with the emulsion graft polymerization system, the GMA conversion rate was high,

exceeding 80%. The variation in the molecular weight of the grafted polymer was measured by gel permeation chromatography, and its crystallinity was investigated with differential scanning calorimetry. The epoxy groups in graft chains were found to be suitable for further chemical modification. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 3575–3581, 2010

Key words: fluoropolymers; functionalization of polymers; graft copolymers; irradiation

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) is a semicrystalline polymer with excellent chemical resistance, thermal stability, processability, and high mechanical properties.^{1,2} These attractive properties have made it an outstanding material for many applications, including coatings,^{3,4} battery separator membranes,^{5–8} separation membranes for industrial waste treatment,^{9–11} and substrate material for biological and medical applications.^{12,13} To improve the performance of PVDF products and exploit their application, there has been great interest in the modification of PVDF, especially in its surface modification via grafting.^{14–16}

In comparison with chemical methods, irradiation-induced graft polymerization can produce a homogeneous grafted polymer without impurities because no chemical additives are used in the initiation.¹⁷ The irradiation methods include preirradiation,^{18,19} simultaneous irradiation,^{20,21} and double irradiation.^{22,23} Grafted polymers can be synthesized from the monomer vapor phase,²⁴ monomer solutions,²⁵ or emulsions.²⁶

The epoxy-group-containing monomer glycidyl methacrylate (GMA) has been widely used to synthesize a precursor for the addition of intended functional polymers by grafting. The grafting of GMA can introduce hydrophilic diol groups into the polymer membrane by the ring-opening reaction of epoxy groups of the poly(glycidyl methacrylate) (PGMA) graft chains under acidic conditions, a technique that reduces the flux decline caused by non-specific protein adsorption onto the hydrophobic polymer.²⁷ Various desired functional groups can be introduced onto the bulk polymer via the addition reaction of epoxy groups and amine derivatives, which is promising for applications of heavy-metal-ion extraction,^{28,29} enzyme immobilization, and specific protein adsorption.^{30,31} Therefore, PVDF grafted with GMA represents a new substrate material with active intermediates and high mechanical properties with the potential for the preparation of functional materials for areas such as heavy-metal-ion extraction and biomedical applications.

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Seko et al.²⁶ grafted GMA onto polyethylene fibers in emulsion instead of using organic solvents and obtained a high degree of grafting (DG), which demonstrated the advantage of the emulsion graft polymerization of oil-soluble monomers. Theoretically, a polymer in powder form is more easily modified via emulsion graft polymerization than its fiber form.

In this study, GMA was grafted onto PVDF powder by preirradiation-induced emulsion graft polymerization. The DG was determined by analysis of the fluorine content by oxygen flask combustion and fluoride-ion-selective electrode methodologies. The kinetics of the graft polymerization was studied, and the chemical structure of the grafted PVDF was determined by Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) analysis. In addition, gel permeation chromatography (GPC) was used to investigate the variation of the molecular weights of PVDF-*g*-PGMAs with different DGs. Finally, the thermal properties of PVDF-*g*-PGMA were investigated by differential scanning calorimetry (DSC).

EXPERIMENTAL

Materials

PVDF was purchased from Solvay Co., Ltd., Brussels, Belgium, in powder form with a particle size of around 0.1 mm. GMA monomer with a purity of 97% or greater was obtained from Sigma-Aldrich Co., St. Louis, Missouri, USA. Tween 20 and other chemical agents were all analytical grade and were purchased from Sino-pharm Chemical Reagent Co., Ltd., Shanghai, P. R. China. All of the materials were used without further purification.

Preirradiation-induced emulsion graft polymerization

PVDF powder was γ -ray irradiated from a ⁶⁰Co source in air at room temperature. Various concentrations of GMA emulsions from 1.5 to 10% were prepared by the addition of the monomer into a 1% Tween 20 solution under stirring. A 10-g sample of the irradiated PVDF powder was added to the emulsion and bubbled with nitrogen gas for 30 min to remove oxygen, and then, the system was heated in a water bath to initiate the graft polymerization. After a definite time, the grafted powder was filtered and washed by water to remove the surfactant and then extracted by methanol in a Soxhlet extractor for 72 h to remove the residual monomer and homopolymer; it was then vacuum-dried for further measurements.

Determination of the DG

Because of the inevitable mass loss of a tiny amount of powder during the experimental operation, it is impos-

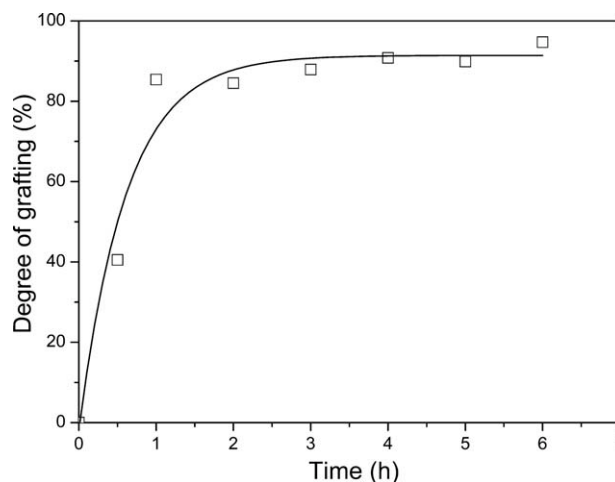


Figure 1 DG of the PVDF-*g*-PGMA powder versus the reaction time. The reaction system consisted of 10 g of preirradiated PVDF powder, 1 mL of Tween 20, 100 mL of water, and 10 mL of monomer. The absorbed dose was 15 kGy, the reaction temperature was 60°C, and the reaction time was from 1 to 6 h.

sible to determine DG by the measurement of the mass increase. Because there was no fluorine in the PGMA graft chain, DG could be calculated from the fluorine content in the grafted PVDF, which was measured by oxygen-flask combustion and fluoride-ion-selective electrode analysis.³² DG was calculated by eq. (1):

$$\text{DG}(\%) = \frac{F_p - F_g}{F_g} \times 100 \quad (1)$$

where F_p and F_g are the fluorine contents in the PVDF powder before and after the grafting copolymerization, respectively.

Measurements

FTIR analysis was performed on a Nicolet Avatar FTIR spectrometer (Thermo Nicolet Instrument Corporation, Wisconsin, USA). The pristine and grafted PVDF powders were pressed into pellets with KBr, and the absorbent spectra were scanned with a step of 4 cm^{-1} .

XPS analysis was performed on a Kratos Axis Ultra DLD XPS instrument (Kratos Analytical Ltd., Manchester, UK) equipped with a monochromated Al $K\alpha$ X-ray source. The polymer powders were vacuum-dried before any measurements were taken.

GPC analysis was performed on a TOSOH HLC-8220 GPC instrument (Tosoh Corp., Tokyo, Japan) with dimethylformamide (DMF; chromatographic grade) as the solvent.

DSC analysis was performed on a Mettler-Toledo 822e DSC instrument (Mettler-Toledo International Inc., Zurich, Switzerland). The analysis of the pristine PVDF

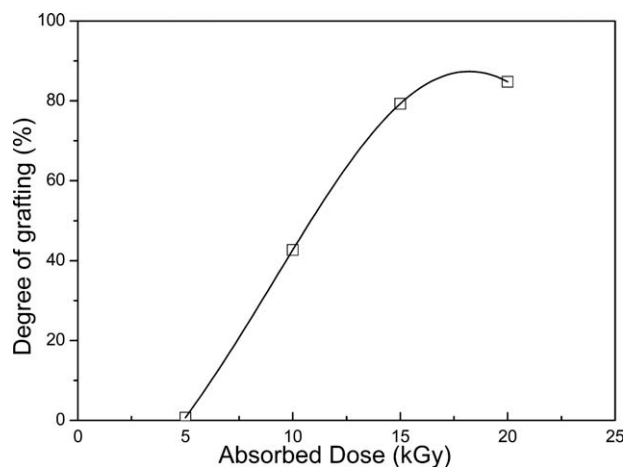


Figure 2 DG of the PVDF-g-PGMA powder versus the absorbed dose. The reaction temperature was 50°C, and the reaction time was 1 h. The other reaction conditions were the same as those in Figure 1.

and PVDF-g-PGMA powders was performed at a heating rate of 20°C/min under a nitrogen gas atmosphere.

The melting point and the degree of crystallization of the pristine PVDF and PVDF-g-PGMA were measured by DSC. The apparent crystallinity was calculated from eq. (2), and the inherent crystallinity of PVDF was calculated from eq. (3):

$$\text{Apparent crystallinity}(\%) = \Delta H_C / 105 \times 100 \quad (2)$$

$$\text{Inherent crystallinity}(\%) = \Delta H_C / \left\{ \frac{1}{1 + \text{DG}} \right\} \times 105 \times 100 \quad (3)$$

where ΔH_C is the crystallization enthalpy (J/g) calculated from the crystallization peak measured by DSC, the value 105 (J/g) is the theoretical crystallization enthalpy of completely crystalline PVDF, and

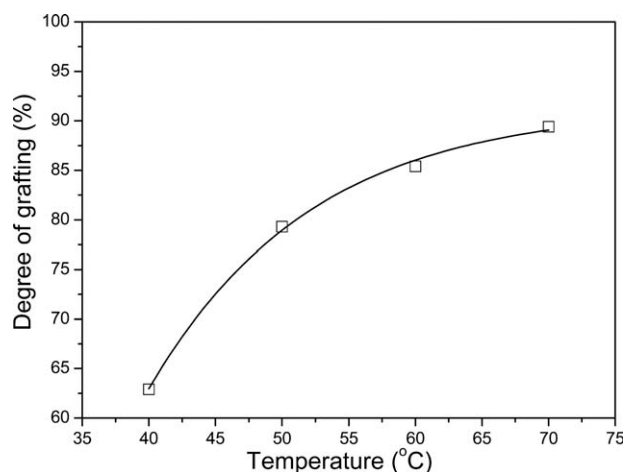


Figure 3 DG of the PVDF-g-PGMA powder versus the reaction temperature. The reaction time was 1 h, the reaction temperature was from 40 to 70°C, and the other reaction conditions were the same as those in Figure 1.

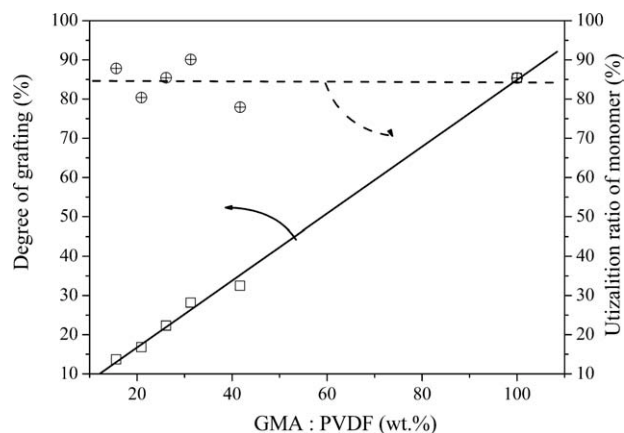


Figure 4 DG of the PVDF-g-PGMA powder versus the feed ratio. The reaction system consisted of 10 g of preirradiated PVDF powder, 1 mL of Tween 20, 100 mL of water, and different amounts of monomer. The reaction time was 1 h, and the other reaction conditions were the same as those in Figure 1.

the value $1/(1 + \text{DG})$ is the weight fraction of PVDF in the grafted powder.

RESULTS AND DISCUSSION

Graft polymerization kinetic study

The kinetics of the emulsion graft polymerization was studied. Figure 1 shows the dependence of the DG of the PVDF-g-PGMA powder on the reaction time. The graft polymerization was found to be very quick, and the DG saturation point was achieved after 1 h. The saturated DG was higher than 90%, which indicated that the utilization ratio of the GMA monomer was also more than 90% because the weight ratio of GMA to PVDF powder was 1. It was obvious that, at 60°C, the emulsion graft

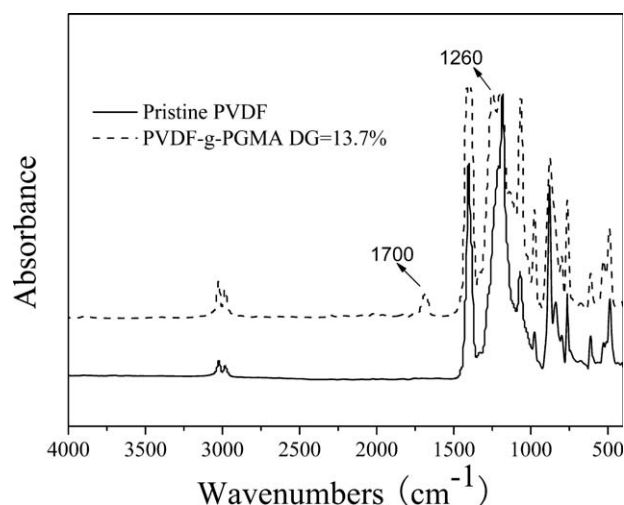


Figure 5 FTIR spectra of (a) pristine PVDF and (b) PVDF-g-PGMA with a DG of 13.7%.

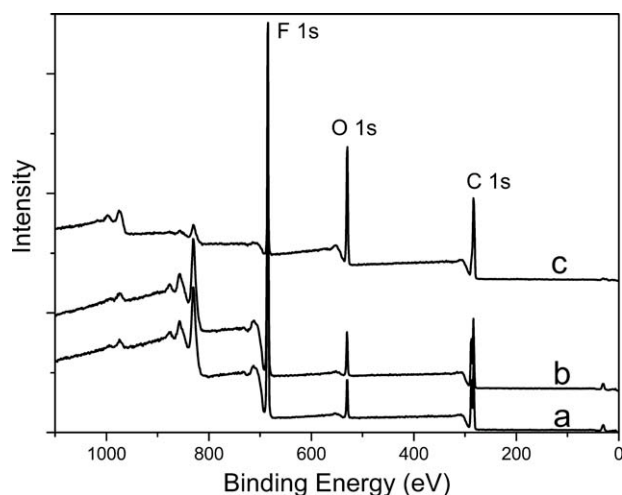


Figure 6 XPS survey spectra of (a) pristine PVDF, (b) irradiated PVDF with an absorbed dose of 15 kGy, and (c) PVDF-g-PGMA with a DG of 48.9%.

polymerization induced by preirradiation was high and showed excellent efficiency. The advantage of the preirradiation-induced graft polymerization method is that the homopolymerization of the monomer is depressed considerably and a high monomer utilization ratio can be obtained.³³ Graft polymerization in emulsion is also more efficient than that in solution.²⁶ The grafting method used in this study was designed with the advantages of both preirradiation and emulsion graft polymerization techniques, and the results indicate that this method would be promising for many applications.

Figure 2 shows the effect of the absorbed preirradiation dose of PVDF on DG of the PVDF-g-PGMA powder. Peroxides and hydroperoxides were introduced onto the PVDF by preirradiation in air. When they were heated, the peroxides and hydroperoxides decomposed to free radicals, which initiated the polymerization. DG of the sample with an absorbed dose of 5 kGy approached zero, which was due to the existence of an inhibitor in the monomer that terminated the radicals because the agent was used without further purification. DG increased with increasing absorbed dose and became saturated when the absorbed dose exceeded 15 kGy.

TABLE I
Elemental Composition Results by XPS Analysis

Sample	C (%)	F (%)	O (%)
Pristine PVDF	43.96	49.73	6.31
Irradiated PVDF with an absorbed dose of 15 kGy	45.37	48.32	6.31
PVDF-g-PGMA (DG = 48.9%)	60.66	12.84	26.50

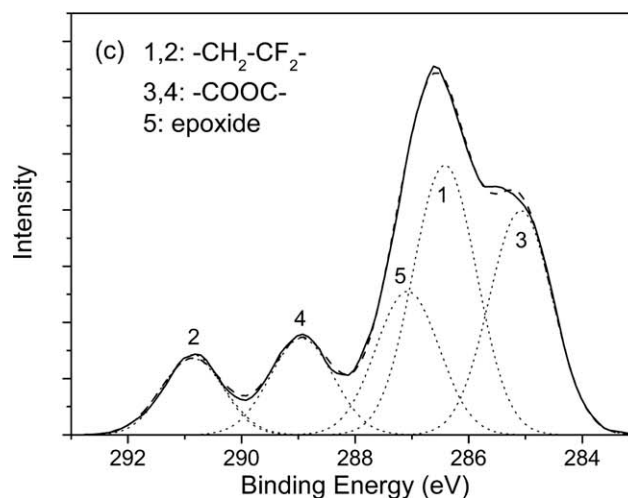
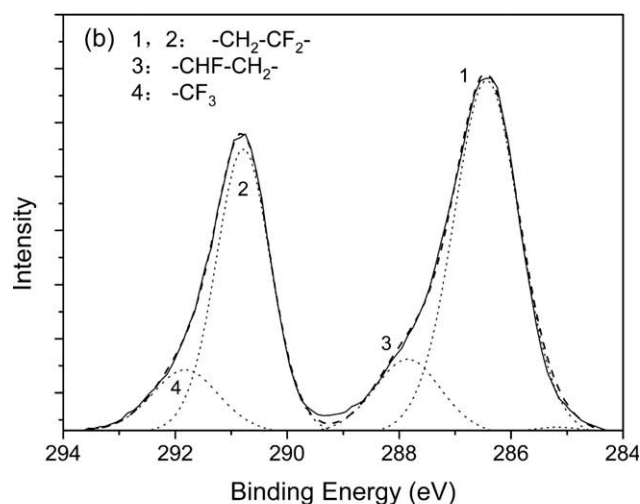
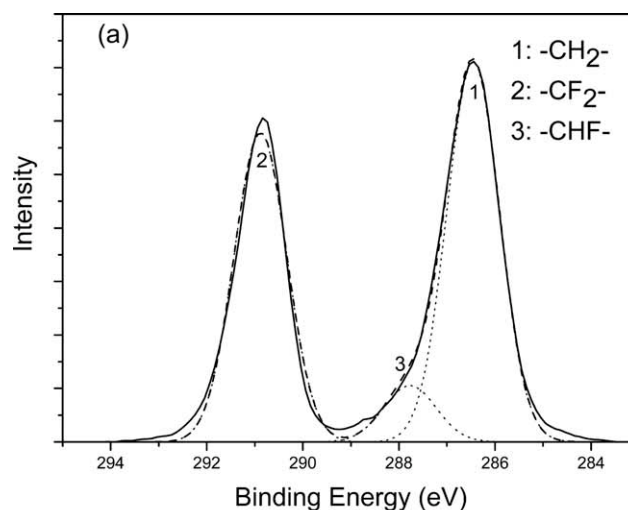


Figure 7 XPS C1s spectra of (a) pristine PVDF, (b) irradiated PVDF with an absorbed dose of 15 kGy, and (c) PVDF-g-PGMA with a DG of 48.9%.

The effect of the reaction temperature on the DG is shown in Figure 3. A higher reaction temperature led to a higher graft polymerization rate, which was in accordance with reported results.³⁴ Because

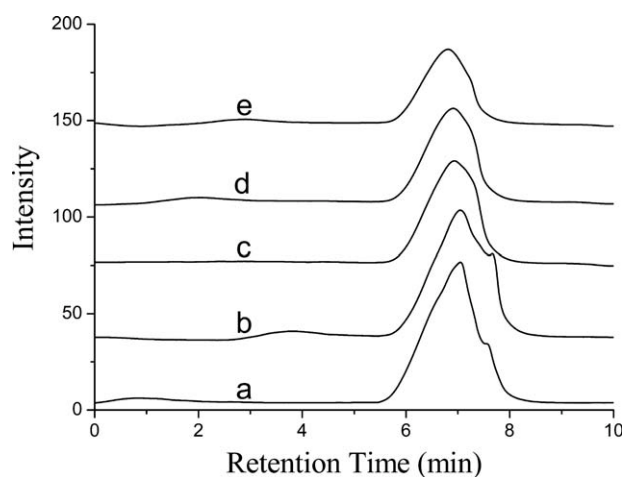


Figure 8 GPC curves of (a) pristine PVDF and (b) irradiated PVDF with an absorbed dose of 15 kGy and PVDF-g-PGMA with DGs of (c) 16.8, (d) 32.5, and (e) 94.3%.

higher temperatures increased the decomposition rate of peroxides and hydroperoxides in producing free radicals, it thus enhanced the graft polymerization rate. Figure 4 shows the effect of the feed ratio of the monomer to PVDF powder on DG. The utilization ratio of monomer was in the range 80–90% when the feed ratio ranged from 15 to 100%, which indicated that the DG could be controlled by the adjustment of the monomer amount with a relatively high utilization ratio of monomer maintained.

Chemical structure analysis

The chemical structures of the PVDF powder before and after grafting were studied by means of FTIR and XPS spectroscopy.

Figure 5 shows the FTIR spectra of pristine PVDF and PVDF-g-PGMA. In the spectrum of the pristine PVDF powder, the absorption bands at 3025 and 2985 cm^{-1} were due to the asymmetric and symmetric stretching vibrations of the $-\text{CH}_2-$ groups, respectively; and the bands at 1402 and 1175 cm^{-1} were attributed to the asymmetric and symmetric stretching vibrations of the $-\text{CF}_2-$ groups, respec-

tively. In the spectrum of the PVDF-g-PGMA, the new band at 1700 cm^{-1} was the stretching vibrations of the carbonyl groups of GMA, and the band appearing at 1260 cm^{-1} was the C—O—C stretching typical of the epoxy ring;³⁵ this indicated the successful introduction of PGMA graft chains onto the PVDF powder.

The XPS wide-scan spectra of the irradiated PVDF and PVDF-g-PGMA powder are shown in Figure 6, and the elemental composition of the samples is shown in Table I. The elements C, F, and O were found in the pristine PVDF powder, where the small amount of O may have been due to contamination from the initials and surfactant, the details of which were not provided by the supplier. After irradiation in air, the percentage of C slightly increased, and the percentage of F decreased; this indicated the breakage of some C—F bonds. After grafting polymerization, the C and O content increased, whereas the F content decreased obviously, which indicated the existence of PGMA graft chains in the PVDF powder. There was still a strong signal for F in the spectrum of the PVDF-g-PGMA powder, and because the probing depth of this XPS instrument was about 5 nm, we concluded that the graft chains could not cover the whole surface of the PVDF powder.³⁶ This meant that the PGMA graft chains were immiscible with PVDF and accumulated on the surface.

The XPS C1s narrow-scan spectra are shown in Figure 7. In the spectrum of pristine PVDF, there were peaks at 286.4 and 290.9 eV, indicating CH_2 and CF_2 groups, respectively. The peak at 287.8 eV was for C—F bonds or C—O bonds which was attributed to the remaining initials and surfactant in PVDF. In the spectrum of the irradiated PVDF, there was a new peak at 291.8 eV for CF_3 end groups in addition to the three peaks attributed to pristine PVDF; this indicated that PVDF decomposed slightly under irradiation. In the spectrum of PVDF-g-PGMA, three new peaks appeared. The peaks at 285.1 and 288.9 eV corresponded to ester groups, and the peak at 287.0 eV corresponded to the epoxy groups,³⁷ which were attributed to the PGMA graft chains.

TABLE II
Molecular Weights of PVDF, Irradiated PVDF, and PVDF-g-PGMA with Different DGs

Sample	High-molecular-weight content				Low-molecular-weight content			
	M_n	M_w	M_w/M_n	Percentage (%)	M_n	M_w	M_w/M_n	Percentage (%)
Pristine PVDF	1.817×10^5	4.166×10^5	2.3	82.8	3.26×10^4	3.65×10^4	1.1	17.2
Irradiated PVDF, 15 kGy	1.380×10^5	3.070×10^5	2.2	77.7	2.77×10^4	3.00×10^4	1.1	22.3
PVDF-g-PGMA, DG = 16.8%	2.001×10^5	3.712×10^5	1.8	79.0	4.41×10^4	5.00×10^4	1.1	21.0
PVDF-g-PGMA, DG = 32.5%	2.290×10^5	4.062×10^5	1.8	78.2	5.22×10^4	5.90×10^4	1.1	21.8
PVDF-g-PGMA, DG = 94.3%	2.717×10^5	4.513×10^5	1.7	81.0	6.57×10^4	7.27×10^4	1.1	19.0

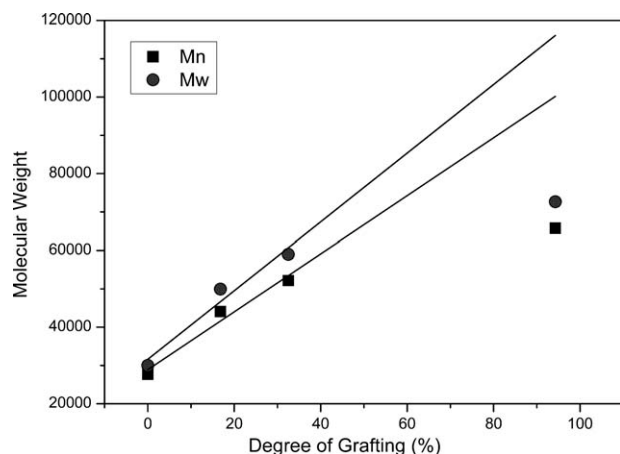


Figure 9 Relationship between the molecular weights and DG of PVDF-*g*-PGMA.

Molecular weight analysis

Figure 8 shows the GPC curves of pristine PVDF, irradiated PVDF with an absorbed dose of 15 kGy, and PVDF-*g*-PGMA with different DGs. The curve of pristine PVDF indicated that the molecular weight of our raw material was doubly distributed with an 82.8% high-molecular-weight part with a weight-average molecular weight (M_w) of 4.166×10^5 and a 17.2% low-molecular-weight part with an M_w of 3.65×10^4 . The detailed data of the molecular weights are listed in Table II.

After irradiation, the molecular weight of both parts of PVDF decreased, which indicated its degradation. After graft polymerization, there were no new peaks in the GPC curves of PVDF-*g*-PGMA, which meant that the homopolymer was thoroughly washed off by extraction. The molecular weights of both parts of PVDF increased with increasing DG, which indicated that there were more PGMA graft chains in PVDF with increasing DG. To better illustrate the relationship between the molecular weights and DG, data are presented in Figure 9 showing that, with a relatively low DG range, both the number-average molecular weight (M_n) and M_w were quite linearly proportional to DG. Only the molecular weights of PVDF-*g*-PGMA with a DG of 94.3% are far from the line. The highly branched structure of the sample accounted for this divergence.

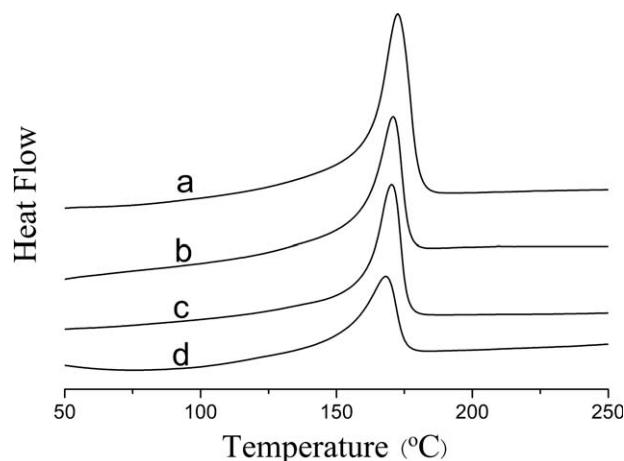


Figure 10 DSC curves of the (a) pristine PVDF and PVDF-*g*-PGMA with DGs of (b) 16.8, (c) 32.5, and (d) 94.3%.

Thermal property measurements

Figure 10 shows the DSC curves of the pristine PVDF and PVDF-*g*-PGMA samples with different DGs. PVDF is a semicrystalline polymer and has a melting temperature around 170°C. The melting peaks of the pristine PVDF and PVDF-*g*-PGMA with different DGs are listed in Table III. For PVDF-*g*-PGMA, the melting temperature decreased slightly to 164°C with increasing DG.

The crystallinity of pristine PVDF and PVDF-*g*-PGMA is shown in Table III. The apparent crystallinity of PVDF-*g*-PGMA decreased with increasing DG. However, when the PGMA weight fraction was deducted because PGMA was amorphous, the inherent crystallinity of the PVDF fraction in PVDF-*g*-PGMA was almost unchanged. The reason was that PGMA and PVDF were incompatible and the PGMA graft chain did not affect the crystal structure of PVDF.

CONCLUSIONS

GMA was grafted onto PVDF powder by preirradiation-induced emulsion graft polymerization, which was designed with the advantages of both preirradiation and emulsion graft polymerization techniques. DG of GMA increased with increasing reaction time, preirradiation dose, reaction temperature, and feed ratio of the monomer. An absorption dose of 15 kGy, a reaction temperature of 60°C, and a reaction

TABLE III
Thermal Properties of PVDF and PVDF-*g*-PGMA with Different DGs

Sample	Pristine PVDF	PVDF- <i>g</i> -PGMA (DG = 16.8%)	PVDF- <i>g</i> -PGMA (DG = 32.5%)	PVDF- <i>g</i> -PGMA (DG = 94.3%)
Melting point (°C)	170.7	169.4	168.4	164.1
Apparent crystallinity (%)	48.9	36.3	36.3	23.0
Inherent crystallinity of the PVDF fraction (%)	48.9	42.4	48.1	44.7

time of 1 h provided the optimal reaction conditions. The results of the graft kinetics indicated that the preirradiation-induced emulsion graft polymerization had excellent efficiency with a high reaction rate and high monomer utilization ratio and offers promise for many applications. The existence of the graft chain was proved by FTIR and XPS spectroscopy. GPC analysis showed that PVDF degraded under irradiation and that the molecular weight of PVDF-g-PGMA increased with increasing DG. The DSC analysis indicated that the grafting of GMA had little effect on the thermal properties of PVDF. The PVDF-g-PGMA powder containing reactive epoxy groups was ready for further functionalization for various applications, such as the preparation of biomaterials and heavy-metal-ion extraction.

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