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Review Article

PVDF-Based Fluoropolymer Modifications via Photoinduced Atom Transfer Radical Polymerizations

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Graft modifications of PVDF fluoropolymers have been identified as the efficient route to improve the properties and expand the applications. Taking advantage of C-F and C-Cl bonds in the repeat units, atom transfer radical polymerizations (ATRP) were widely used for graft modification. Recently, photoinduced ATRP has shown good spatial and temporal control over the polymerization process in contrast to thermal activation mode. This minireview highlights the progress in PVDF-based fluoropolymer modifications by using photoinduced Cu(II)-mediated ATRP and organocatalyzed ATRP. The challenges and opportunities are proposed with the aim at advancing the development of synthesis and applications of fluoropolymer.

1. Introduction

Poly(vinylidene fluoride) (PVDF) and PVDF-based fluoropolymers exhibit unique chemical and physical properties, which are widely used as membrane and dielectric materials [1–3]. In order to further enhance their performances and expand the applications, functionalization of PVDF-based fluoropolymers has been paid much attention from both academia and industry, such as copolymerization with functional monomers and graft modification via reversible-deactivation radical polymerization (RDRP) [4]. Among them, in the benefit of C-F and C-Cl bond in the repeat units, atom transfer radical polymerization (ATRP) has been utilized to introduce different side chains into the PVDF-based fluoropolymer to improve the solubility, compatibility, and functionality [5].

Since the discovery in 1995, ATRP has been developed as one of the most powerful RDRP strategies for the preparation of well-defined macromolecules [6, 7]. Significant advances in catalysis system have been achieved for ATRP

[8]. The initial catalyst for ATRP is Cu(I) but the concentration is high ([Initiator]: [Cu(I)] = 1 : 1) in order to compensate for unavoidable radical termination reactions [9]. Subsequent efforts were made to develop improved ATRP systems to decrease the catalyst loading and increase the control level, such as activators regenerated by electron transfer (ARGET) ATRP [10], initiators for continuous activator regeneration (ICAR) ATRP [11], electrochemically-mediated ATRP (eATRP) [12], and single-electron transfer radical polymerization (SET-LRP) (also termed as supplemental activator and reducing agent (SARA) ATRP) [13, 14].

The switch from thermal mode into photoactivation represents a big step forward in polymer chemistry [15]. Under the exposure of the light, Cu(II), iridium, and ruthenium complexes are served as the photocatalyst for ATRP to activate the initiator to generate the radicals [16, 17]. Low metal catalyst loading and good temporal and spatial control bring about vast opportunities in polymer synthesis. The emerging organocatalyzed ATRP (O-ATRP) achieves metal-free polymer products, which attracts growing interest and shows
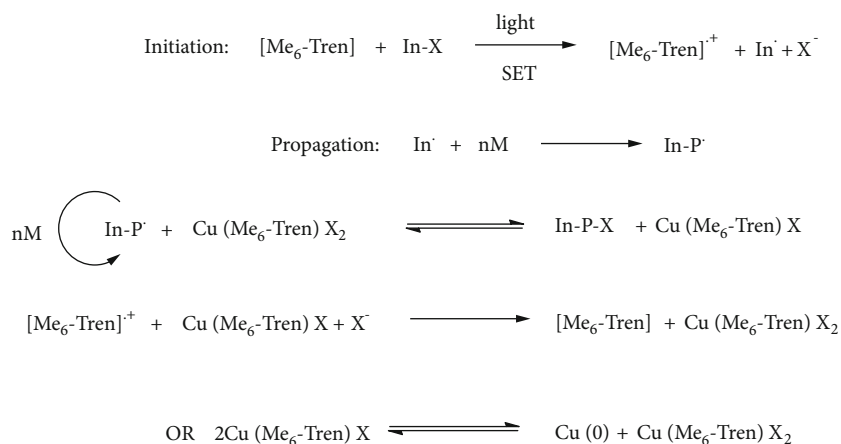
Initiation: $[Me_6\text{-}Tren]$ + In-X $\xrightarrow[\text{SET}]{\text{light}}$ $[Me_6\text{-}Tren]^{\cdot+}$ + In$^{\cdot}$ + X^{-}

Propagation: In$^{\cdot}$ + nM $\longrightarrow$ In-P$^{\cdot}$

nM $\circlearrowleft$ In-P$^{\cdot}$ + Cu $(Me_6\text{-}Tren)$ X$_2$ $\rightleftharpoons$ In-P-X   + Cu $(Me_6\text{-}Tren)$ X

$[Me_6\text{-}Tren]^{\cdot+}$ + Cu $(Me_6\text{-}Tren)$ X + X^{-} $\longrightarrow$ $[Me_6\text{-}Tren]$ + Cu $(Me_6\text{-}Tren)$ X$_2$

OR   2Cu $(Me_6\text{-}Tren)$ X $\rightleftharpoons$ Cu (0) + Cu $(Me_6\text{-}Tren)$ X$_2$

FIGURE 1: Mechanism of photoinduced Cu(II)-mediated ATRP [36].
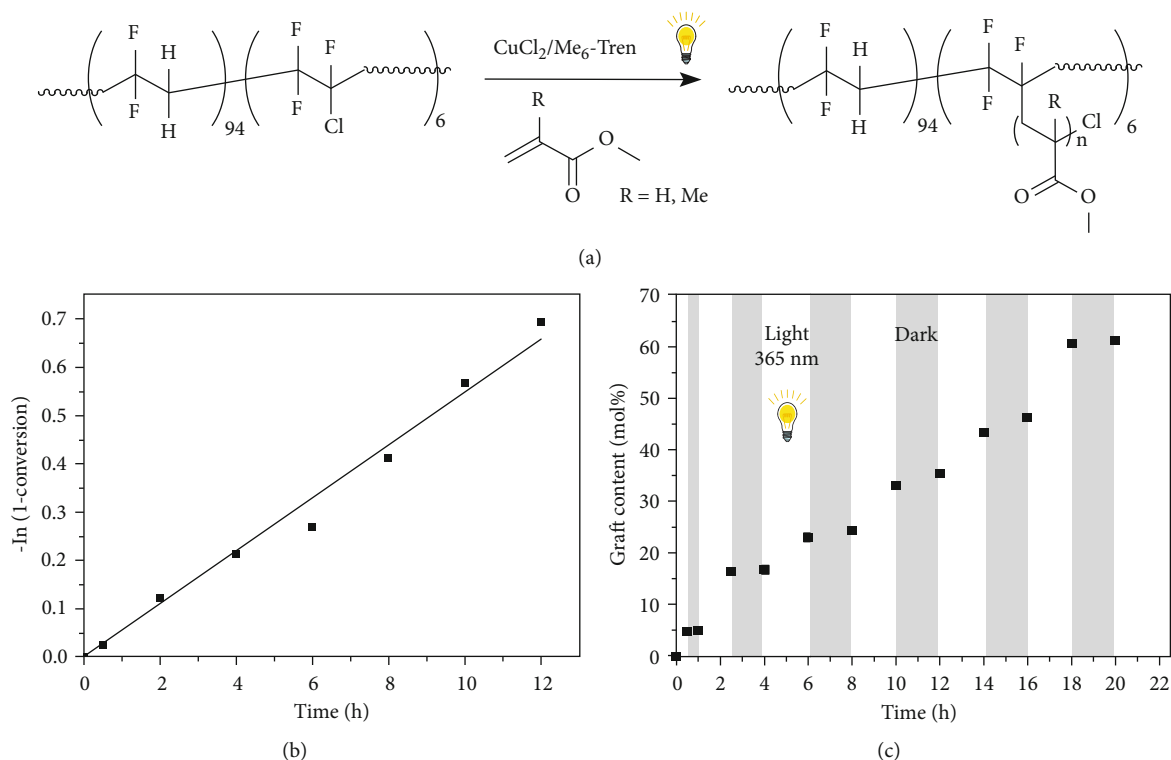

(a)

(b)

(c)

FIGURE 2: (a) Graft modification of P(VDF-co-CTFE) via photoinduced Cu(II)-mediated ATRP; (b) semilogarithmic kinetic plots for photoinduced Cu(II)-mediated RDRP of MMA ([Cl]: [Cu]: [L]: [M] = 1 : (1/32): (6/32): 30, UV (λ_{max} = 365 nm)); (c) graft contents vs. reaction time dependence for photoinduced Cu(II)-mediated RDRP of MMA under "on-off" UV sequence ([Cl] : [Cu] : [L] : [M] = 1 : (1/32) : (6/32) : 30, UV (λ_{max} = 365 nm)) [38].

significant applications in fabrication biomedical and electronic materials [18–20].

The original graft modification of PVDF-based fluoropolymer was reported via thermal-activated ATRP [5]. Cu(I)- and Cu(0)-promoted graft ATRP was presented in the batch reactor and continuous flow microreactor [21–24]. Later, photoinduced ATRP was applied in PVDF-based fluoropolymer modification. This minireview briefly summarizes thermal-activated ATRP modification and then highlights recent progress in photoinduced ATRP graft from

PVDF-based fluoropolymers. We hope that it would provide guidance for fluoropolymer synthesis and application.

2. Modification via Thermal-Activated ATRP

At the elevated temperatures, Cu(I)/ligand-mediated ATRP was initially employed to synthesize poly(vinylidene fluoride-co-chlorotrifluoroethylene) (P(VDF-co-CTFE)) graft copolymers [5, 25–28]. Although the dielectric properties of the resultant copolymers were improved, unexpected

TABLE 1: Results of P(VDF-*co*-CTFE) initiated photoinduced Cu(II)-mediated RDRP [38].

Run	M	[Cl]:[Cu]:[L]:[M]	Time (h)	Conversion (%)[a]	Graft content[b]	Graft length[c]	$M_{\text{n,NMR}}$ (g/mol)[d]
1	MMA	1:(1/32):(2/32):30	6	14.8	22.8	3.8	8880
2	MMA	1:(1/32):(4/32):30	6	17.6	27.5	4.6	9350
3	MMA	1:(1/32):(6/32):30	6	39.9	65.5	10.9	13150
4	MMA	1:(1/32):(8/32):30	6	31.2	50.9	8.5	11690
5	MMA	1:(1/64):(6/64):30	6	31.9	52.5	8.8	11850
6	MMA	1:(1/128):(6/128):30	6	27.9	46.3	7.7	11230
7	MMA	1:(1/256):(6/256):30	6	25.8	41.2	6.9	10720
8	MMA	1:(1/512):(6/512):30	6	25.4	42.2	7.0	10820
9	MMA	1:(1/1024):(6/1024):30	6	25.1	41.2	6.9	10720
10	MMA	1:(1/32):(6/32):30	12	64.4	87.2	14.5	15320
11	MMA	1:(1/32):(6/32):50	12	54.6	121.4	20.2	18740
12	MMA	1:(1/32):(6/32):80	12	46.9	173.6	28.9	23960
13	MMA	1:(1/32):(6/32):100	12	45.8	201.4	33.6	26740
14	MA	1:(1/32):(6/32):30	6	19.8	31.6	5.3	9760

[a]Conversion was calculated by ^{1}H NMR, [b]graft content was calculated by ^{1}H NMR after extraction, [c]graft length equaled graft content divided by 6, [d]$M_{\text{n,NMR}}$ was calculated by combination of graft content, molecular weight of monomer, and P(VDF-*co*-CTFE) ([VDF]:[CTFE] = 94 : 6).
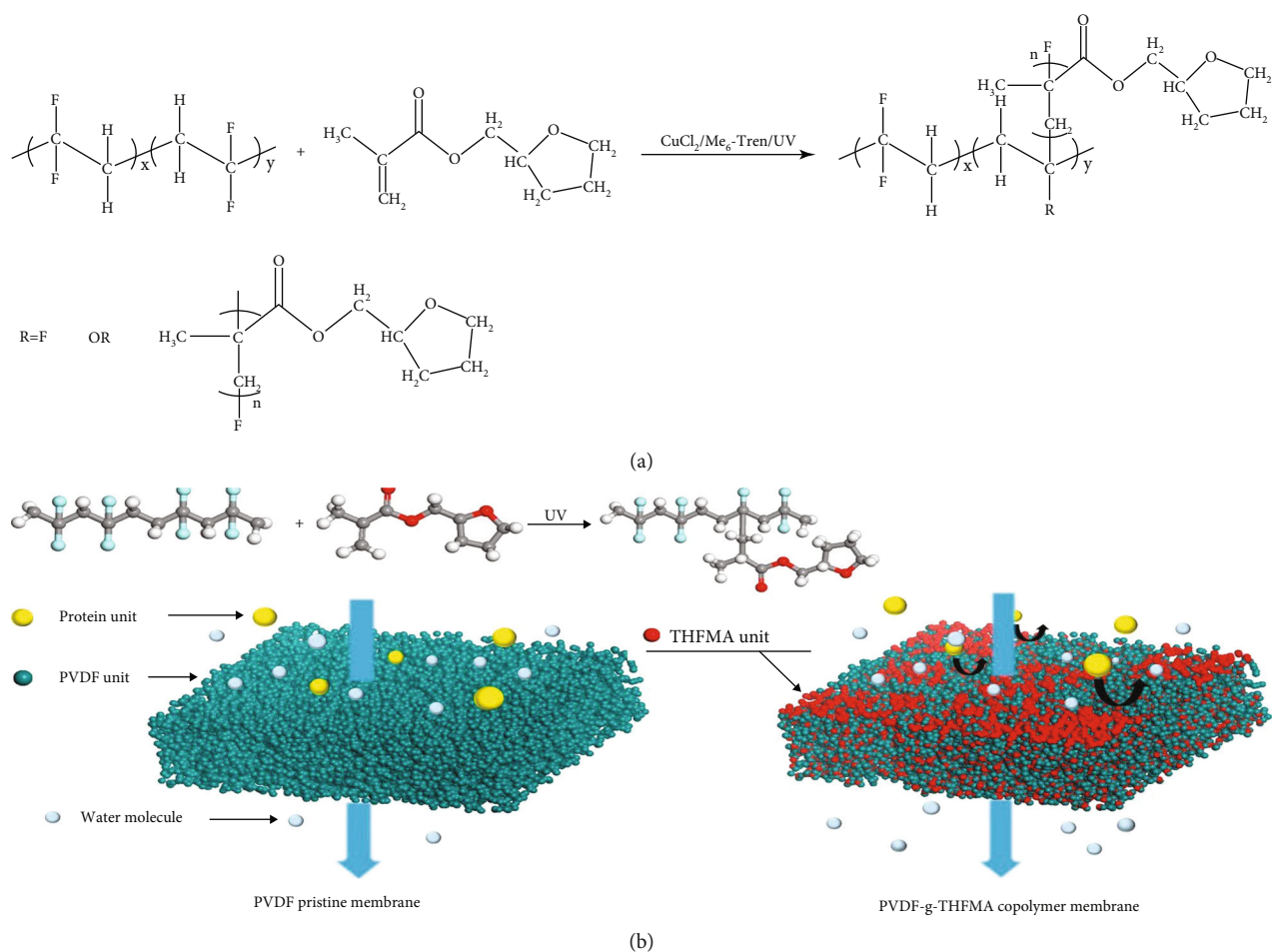

(a)

(b)

FIGURE 3: (a) Graft modification of P(VDF) via photoinduced Cu(II)-mediated ATRP; (b) comparison between PVDF pristine membrane and PVDF-*g*-THFMA copolymer membrane [40].
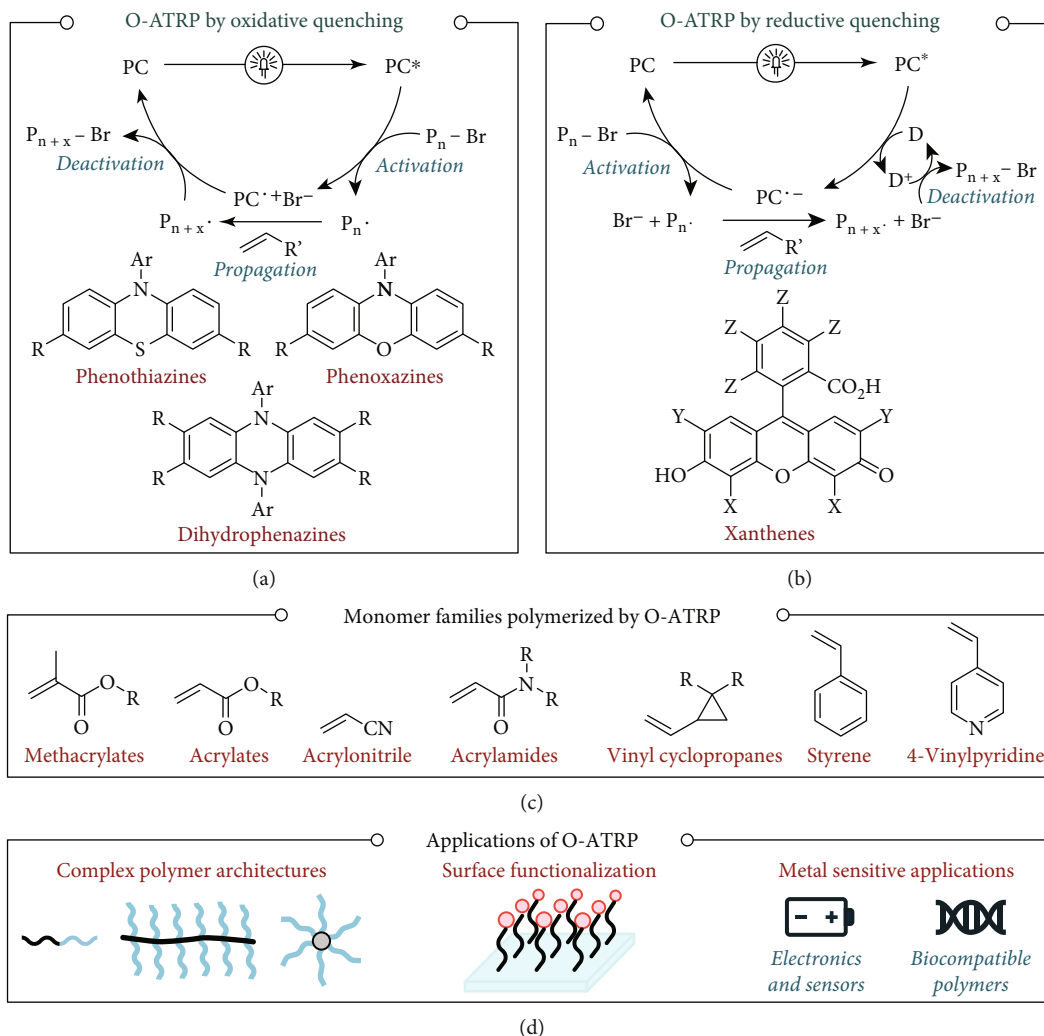
FIGURE 4: Overview of O-ATRP: (a) the mechanism of O-ATRP by oxidative quenching and common PCs employed therein, (b) the mechanism of O-ATRP by reductive quenching and a common PC family employed in this method, (c) monomer families that have been polymerized by O-ATRP, and (d) common applications of O-ATRP [18].

chain transfer reactions and dehydrochlorination side reactions occurred, which was attributed to the large copper loading (equivalent to C-Cl initiator) and high reaction temperature. Alternatively, Cu(0) as catalyst enabled lower copper concentration and mild reaction conditions [29–32]. By using Cu(0) catalysis system (1/4 equivalent Cu(0) to initiator), colorless P(VDF-co-CTFE) graft copolymers were prepared [21–23]. Moreover, copper tubular reactor provided additional benefits for graft modification, such as faster polymerization, suppressed "hot spot" effects, and decreased ligand feeding [24].

3. Modification via Photoinduced Cu(II)-Mediated ATRP

Photoinduced ATRP was pioneeringly investigated by Yagci [33], Hawker [34], Matyjaszewski [35], and Haddleton [36]. Cu(II) together with tertiary amine showed excellent control of acrylate polymerization under 365 nm UV irradiation.

The polymerization mechanism of Cu(II)-mediated RDRP was proposed in Figure 1 [36]. By using Cu(II)-mediated ATRP, heterofunctional polyacrylates, water soluble polymers, and block copolymers were prepared with high efficiency and good control [37].

Hu et al. explored photoinduced Cu(II)-mediated ATRP of MMA in the presence of P(VDF-co-CTFE) as the macroinitiator (Figure 2(a)) [38]. In contrast to the traditional ATRP process by using Cu(I) as the catalyst (equal equivalent Cu(I) to Cl atom), the catalyst loading of Cu(II) was decreased into 1/128 equivalent with good performance for P(VDF-co-CTFE)-initiated MMA polymerization. The Cu(II) concentration could be as low as 1/1024 equivalent (Table 1). Another benefit by using photoinduced Cu(II)-mediated RDRP was that graft content of PMMA was much higher than traditional ATRP or SET-LRP. Under optimal reaction conditions, 121.4-201.4 mol% was achieved (Table 1), which was the largest value for graft modification of P(VDF-co-CTFE). Kinetics study confirmed the linear dependence of -ln(1-conversion)
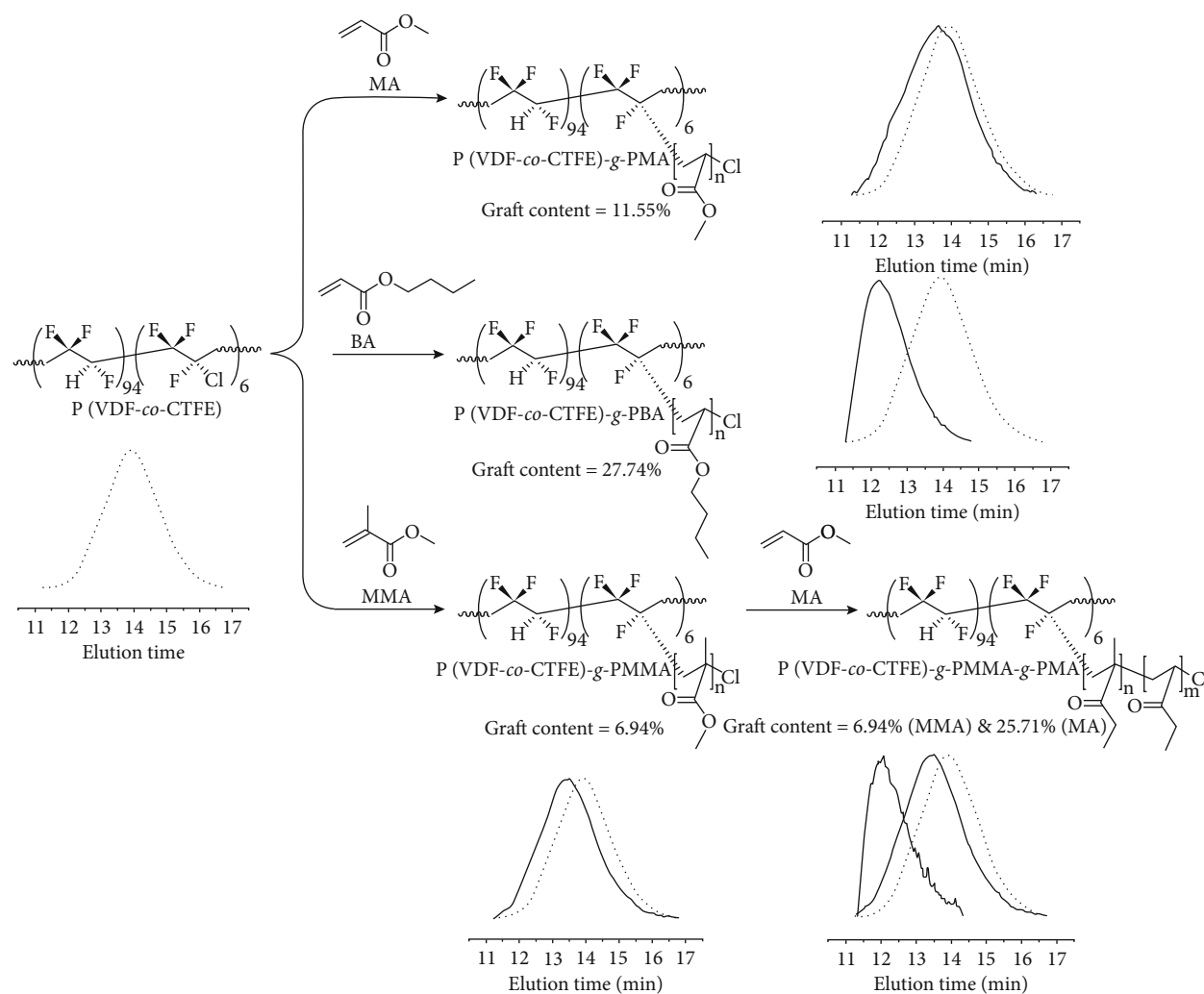
Figure 5: Photoinduced PTH catalyzed O-ATRP synthesis of P(VDF-co-CTFE)-g-PMA ($M_{n,SEC}$ = 141000, $Đ_M$ = 3.51) ([Cl] : [PTH] : [MA] = 1 : 0.125 : 10, 6 h), P(VDF-co-CTFE)-g-PBA ($M_{n,SEC}$ = 214300, $Đ_M$ = 3.28) ([Cl] : [PTH] : [BA] = 1 : 0.125 : 50, 12 h), and P(VDF-co-CTFE)-g-(PMMA-b-PMA) ($M_{n,SEC}$ = 221000, $Đ_M$ = 3.02) ([Cl] : [PTH] : [MMA] = 1 : 0.125 : 10, 6 h; [Cl] : [PTH] : [MA] = 1 : 0.125 : 10, 6 h) [43].

on time, which indicated that polymerization rate is to be the first order in monomer concentration (Figure 2(b)). Compared to the thermal-activated mode, photochemistry allowed for temporal control of polymerization process. By turning the light "on" and "off," graft polymerization went and stopped, which showed good light responsive nature (Figure 2(c)). Through this efficient graft medication strategy, P(VDF-co-CTFE)-g-PMMA, P(VDF-co-CTFE)-g-PMA, P(VDF-co-CTFE)-g-PAN, and P(VDF-co-CTFE)-g-(PMMA-b-PMA) were prepared [39].

C-F bond was also effective to initiate polymerization. Lei et al. investigated photoinduced Cu(II)-mediated RDRP of tetrahydrofurfuryl methacrylate (THFMA) by using PVDF as the macroinitiator (Figure 3(a)) [40]. By incorporating relatively more hydrophilic segments of PTHFMA compared with PVDF, the grafted modified membranes showed good antifouling property and filtration performance (Figure 3(b)). A pure water flux of 293.9 L/m2/h/bar and a molecular weight cutoff of 39.5 Kda were achieved. After filtration and washing by deionized water, the PVDF-

g-PTHFMA membrane exhibited a recovery ratio of the pure water flux of 89.1%.

4. Modification via Photoinduced O-ATRP

Photoinduced Cu(II)-, Ir-, and Ru-mediated ATRP inspired the use of organic photoredox catalyst. In 2014, the first example of organocatalyzed metal-free ATRP (O-ATRP) was reported by Fors and Hawker (N-phenylphenothiazine (PTH)) [41] and Miyake and Theriot (Perylene) [42], respectively. Until now, a series of organocatalysts via oxidative quenching (Figure 4(a)) or reductive quenching path (Figure 4(b)), varied vinyl monomers (Figure 4(c)), and related applications (Figure 4(d)) have been investigated and nicely reviewed [18].

Hu et al. employed PTH as a model organocatalyst to conduct O-ATRP modification of poly(vinylidene fluoride-co-chlorotrifluoroethylene) (P(VDF-co-CTFE)) [43]. Both ^{1}H NMR and ^{19}F NMR demonstrated that less active C-Cl bond in P(VDF-co-CTFE) acted as the initiator for O-ATRP
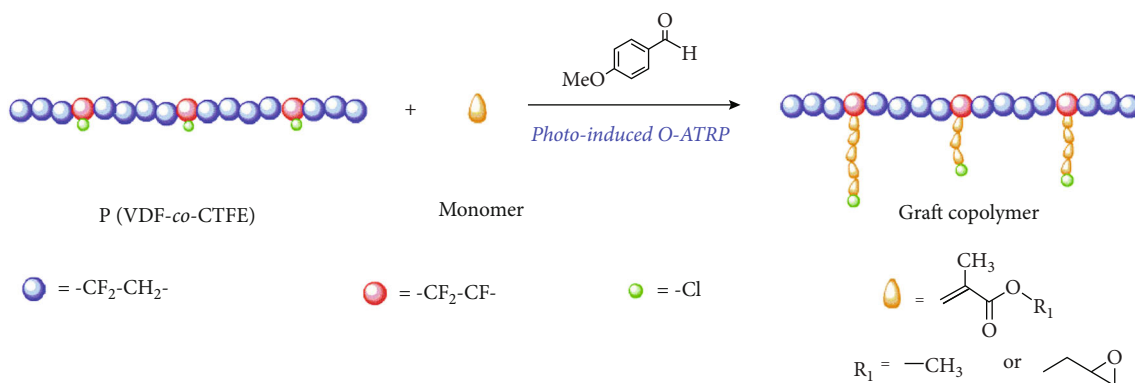
FIGURE 6: Photoinduced *p*-anisaldehyde catalyzed O-ATRP synthesis of P(VDF-*co*-CTFE)-*g*-PMMA and P(VDF-*co*-CTFE)-*g*-PGMA [44].

of methyl methacrylate (MMA) under 6 h 365 nm UV irradiation. The advantage of temporal control for photochemistry enabled graft modification "on" and "off" by switching the UV irradiation. The graft contents of PMMA were varied from 4.69 mol% to 37.67 mol% through regulating the reaction conditions. A series of P(VDF-*co*-CTFE)-*g*-PMA, P(VDF-*co*-CTFE)-*g*-PBA, and P(VDF-*co*-CTFE)-*g*-PMMA-*g*-PMA were obtained by expanding the monomer scope and performing chain extension experiment (Figure 5).

Hu et al. developed *p*-anisaldehyde as the photoredox catalyst for photoinduced O-ATRP in the presence of P(VDF-*co*-CTFE) as the macroinitiator (Figure 6) [44]. The catalyst loading was one-fifth lower than PTH (0.025 eq vs. 0.125) for MMA graft polymerization. Besides PMMA, 5.09-12.69 mol% poly(glycidyl methacrylate) (PGMA) was incorporated into the fluoropolymers under 8 h UV irradiation. Thermal property study showed that the crystallinity and the crystal domain size were reduced by attaching the graft chains into fluoropolymer backbone. The functional epoxy groups in GMA provided opportunities for postmodification. In the benefit of using organocatalyst, metal catalyst contamination was avoided in the resultant fluoropolymers. It was demonstrated that metal-free P(VDF-*co*-CTFE)-*g*-PMMA exhibited reduced dielectric loss at low frequency and high temperature, decreased conduction loss, and enhanced breakdown strength [45].

O-ATRP was also used for hydrogenation of P(VDF-*co*-CTFE) to prepare P(VDF-*co*-TrFE) and P(VDF-*co*-TrFE-*co*-CTFE) [46]. The C-Cl bonds in P(VDF-*co*-CTFE) were activated by PTH under the exposure of UV. In the absence of monomer, the generated macroradicals transferred into either polar solvent or other reagents. As a result, CTFE units were partly or all converted into TrFE. This organocatalyzed atom transfer radical chain transfer reaction provided an alternative modification strategy for fluoropolymers.

5. Conclusion

Graft modifications of PVDF-based fluoropolymers have achieved great progress with improved properties and expanded applications. To the best of our knowledge, 7 papers have been published in this related field [38–40, 43–46]. Photoinduced ATRP showed remarkable priorities

in contrast to thermal-activated ATRP (Cu(I) and Cu(0)), including but not limited to (1) spatial and temporal control over polymerization process, (2) lower catalyst loading, (3) higher graft contents, and (4) metal-free grafted polymers (O-ATRP). The current results indicated that the catalyst concentration and control level should be improved further for O-ATRP graft modification of PVDF-based fluoropolymers. Recently, a series of powerful organocatalysts have been presented with 1-10 ppm catalyst loading and high activity toward more monomer polymerization [47, 48], which will be a good candidate to be applied to graft modification. C-F bond-initiated polymerization should be deeply investigated, and the fluoropolymers should be expanded from PVDF and P(VDF-*co*-CTFE) to more fluorinated polymers. We believe that high-performance fluoropolymers will be prepared by using photoinduced ATRP and applied in many interesting fields in the future.

Conflicts of Interest

The author(s) declare(s) that they have no conflicts of interest.

Authors' Contributions

J. D. and X. H. were responsible for the conceptualization, funding acquisition, and writing of the original draft and review and editing; H. Z., P. L., L. S., Y. L., D. J., N. X., and G. P. were responsible for writing the original draft and review and editing; C. L., Z. X., N. Z., and K. G. were responsible for the conceptualization, funding acquisition, project administration, resources, supervision, and writing (review and editing). N. X. and G. P. contributed equally to this work.

Acknowledgments

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