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AGC Comments Addendum (Copies of Studies) -- Vol. 31

Table 9

Properties and performances of PVDF membrane modified by blending.

Blending	PVDF membrane	Pure water flux (L/m ² h)	Rejection	Water flux recovery	Contact angle (°)	Additives
Original	PVDF Kynar-460, 20%	0.35 L cm ⁻² min ⁻¹	0.106 μm ^a		80	PVP, flat sheet [84]
Modified	PVP 7.5%	0.68 L cm ⁻² min ⁻¹	0.22 μm ^a		78	
Original	PVDF 12.8%	9.25 (0.1 MPa)	83.34%			PVP, hollow fibre [183]
Modified	PVP 3%	440 (0.1 MPa)	77.24%			
Original	PVDF 10%	(1 bar)				PEG, flat sheet [11]
Modified	PEG 2.5%	4 × 10 ³ ml/cm ² s	75–80% ^b			
Original	PVDF 19%	1.3 (1 bar)	55 ^c		80	PMMA, flat sheet [184]
Modified	PMMA 5%	209 ± 120 (1 bar)	38 ± 19 ^c		68	
Original	PVDF 18%	31.8 (276 kPa)	~20% ^d			P(MMA-r-POEM), flat sheet [185]
Modified	P(MMA-r-POEM) 2%	48.2–166.2	~20% ^d			
Original	PVDF 16%	106.3				P(MMA-r-POEM), hollow fibre [186]
Modified	P(MMA-r-POEM) 3.2%	693.0	128 nm ^e	86.6%	15s ^f	
Original	PVDF 18%				89.9	PVDF-g-POEM, ATRP, flat sheet [182]
Modified	PVDF-g-POEM, 2%				53.5	
Original	PVDF 18%					PVDF-g-PMAA, ATRP, flat sheet [187]
Modified	PVDF-g-PMAA 2%	507–29.0				
Original	PVDF	10 (0.1 bar)	63–97 nm			PVDF-g-PTMSPMA, ATRP, flat sheet [188]
Modified	PVDF-g-PTMSPMA	80–100 (0.1 bar)	130–175 nm			
Original	PVDF	~160 ^g			124	PVDF-g-PEGMA, RAFT [189], thermal
Modified	PVDF-g-PEGMA	360 ^g	0.5 μm ^h		34	[190], flat sheet
Original	PVDF 10%	~50 (0.1 MPa)	99% ^d	22%	92	HPE-g-MPEG, flat sheet [191]
Modified	HPE-g-MPEG 3%	~600 (0.1 MPa)	92% ^d	89%	49	
Original	PVDF 12%, PT12-0-FW	310	0.2 μm ⁱ		72.5	TiO ₂ , flat sheet [129]
Modified	TiO ₂ 2%, PT12-0-FW	300	0.125 μm ⁱ		68	
Original	PVDF 15%	303	93% ^j		86.7	TiO ₂ , flat sheet [192]
Modified	TiO ₂ /PVDF = 0.3	331	95% ^j		81.1	
Original	PVDF M3	~750	94.4% ^d	28.2%	85	TiO ₂ , flat sheet [125]
Modified	PVDF-TiO ₂ M3 (Ti)	~750	88.8% ^d	80.5%	54.1	
Original	PVDF 18%	~80	0.074 μm ^k		82.9	SiO ₂ , hollow fibre [127]
Modified	SiO ₂ sol 3%	301	0.099 μm ^k		53.4	
Original	PVDF 19%	52.0	95.5%	88.5%	83.6	Al ₂ O ₃ , flat sheet [121,193]
Modified	Al ₂ O ₃ 2%	74.3	96.5%	91.5%	57.4	

^a Mean pore radius of the membrane measured by gas permeation method.^b Rejection of 1% aqueous solution of PVA 205 for membranes treated in hot water.^c Rejection of 5% aqueous solution of PEG 35,000.^d Rejection of BSA solution with the molecular weight 67,000.^e Carbon ink particles above 128 nm can be rejected by the membrane.^f The contact angle of the inner surface of hollow fibre #7 drops from 82° to 0° in 15 s.^g Permeation of 1 g/L γ-globulin solution after 600 s.^h Mean pore size measured on Coulter Porometer II.ⁱ Mean pore size measured by a microflow porometer.^j Rejection of PEO MW 100,000.^k Mean pore radius determined by filtration velocity method.

4.1.2.4. “Living”/controlled polymerisation grafting. Recently, “living” polymerisations, including anionic and cationic polymerisations, have been used to graft copolymer on a solid surface [171–173]. Unlike the strict reaction condition required for ionic polymerisations, for example, complete absence of water, limited the choice of monomer, “living”/controlled free radical polymerisations combine ease of polymerisation and a large number of monomers capable of reaction. It has the advantage of living ionic polymerisation for a better control, with the versatility and convenience of the free radical polymerisation [174,175].

Atom transfer radical polymerisation (ATRP) and reversible addition-fragmentation chain transfer polymerisation (RAFT) are most widely used to graft chains or brushes onto the PVDF membrane surface. The key reaction mechanisms have been thoroughly discussed in previous publications. For example, the structure–reactivity correlations, the transfer of a halide atom

from a catalyst/ligand complex to a propagating macro-radical in ATRP, rules for the catalyst selection in ATRP [176,177], addition of propagating macro-radicals to the carbon sulphur double bond of a RAFT reagent, rules for the chain transfer agent selection in RAFT, etc. have been explored by many researchers in recent years [178,179].

In this part, emphasis is placed on the surface modification applications of ATRP and RAFT methods on the PVDF porous membranes. Both methods are able to design and manipulate the structure and length of the grafted chains on the membrane surface, which as a result, are able to tune the pore size and the pore size distribution and avoid pore plugging [180]. Furthermore, ATRP and RAFT could produce more uniform and smooth surfaces than conventional radical polymerisation, which is an important factor in the adsorption fouling of protein during the micro- or ultra-filtration process. The choice of solvent for the surface grafting on PVDF membrane surface is crucial. On one hand, it should facilitate

the successful controlled copolymerisation of grafted chains; on the other hand, it should keep the integrity of the bulk membrane without destroying or dissolving the membrane. The development of controlled/living radical polymerisation in aqueous systems has enabled its application in the surface grafting on the PVDF membrane surface directly using water-borne system as the reaction medium [181].

The PVDF membrane is well-known for the excellent resistance to chemicals and oxidants due to the high carbon–fluoride bond strength, so the PVDF membrane with alkyl fluorides had not been widely used as ATRP initiators in earlier days. Therefore, surface initiators are usually immobilised onto the PVDF membrane surface prior to grafting. To activate the PVDF membrane, poly(glycidyl methacrylate) (PGMA) was coated on the PVDF membrane to form a reactive primary polymer layer, and then reaction of vapour-phase bromoacetic acid with the remaining epoxide groups of PGMA produced tethered bromoacetate groups capable to initiate ATRP of 2-vinylpyridine on the PVDF membrane in the organic solvent of acetonitrile [157]. It is possible to tune the pore size, pore size distribution and ion-exchange capacity using polymerisation time as an independent variable because of the linear relationship between the grafting degree of polymer chain and “living”/controlled polymerisation time.

Surface initiators can also be immobilised on the PVDF membrane by surface hydroxylation and esterification of the hydroxyl groups covalently linked to the surface with 2-bromoisobutyrate bromide. Thereafter, polymer brushes of methyl methacrylate (MMA) and poly(ethylene glycol) monomethacrylate (PEGMA) were grafted onto the PVDF membrane surface by ATRP [158]. X-ray photoelectron spectroscopy (XPS), attenuated total reflectance (ATR-FTIR) spectroscopy and contact angle can characterise the presence of surface grafted polymer brushes. Because of the higher active property of alkyl bromide bonding in the initiation of ATRP, bromide can be introduced onto the PVDF membrane via the O_3/O_2 treatment and subsequent bromination reaction [159,160]. The PVDF membranes grafted by poly(sulfobetaine methacrylate) (PSBMA) and PEGMA exhibited better anti-fouling for BSA filtration. Moreover, it was also reported that network-like PEGMA on the PVDF membrane surface adsorbed less BSA than brush-like PEGMA because of the higher hydration capacity [160].

However, in order to avoid the complicated multi-steps of immobilizing initiators on the PVDF membrane and indirect grafting polymerisation, the first example using PVDF as macro-initiator to obtain amphiphilic graft copolymer for membrane applications was developed by Mayes and co-workers [182]. The most attractive attribute of this polymerisation route is the nature of PVDF as the macro-initiator. PVDF is an organic halide which can act as an ATRP macro-initiator, enabling the facile grafting of vinyl side chains directly onto PVDF.

Chen et al. achieved the surface grafting copolymerisation of 2-(N,N-dimethylamino)ethyl methacrylate (DMAEMA) and poly(ethylene glycol) monomethacrylate (PEGMA) on the PVDF membrane using ATRP in medium of distilled water [161]. To confirm the living nature of ATRP, PVDF membrane with already existed graft polymer brushes was further grafted by styrene using ATRP to form diblock copolymer brushes on the PVDF surface. Both homopolymer and diblock copolymer covalently tethered to the PVDF surface imparted new and well-structured functionalities directly onto the PVDF membrane, which demonstrated good antifouling properties.

However, the halide species, $R\cdot$, is usually toxic and the catalyst/ligand complex is easily oxidized by the dissolved oxygen in the solution. To overcome these drawbacks, a reverse atom transfer radical polymerisation (RATRP) has been explored to modify the PVDF membrane surface. RATRP is different from ATRP in its

initiation process, where a conventional radical initiator, such as BPO, is used instead of the organic halide initiator. The PVDF membrane was first treated by UV irradiation and then exposed to the air to produce peroxide and hydroperoxide on the membrane surface, which were used for the subsequent surface-initiated reverse atom transfer radical polymerisation (RATRP) in toluene [162]. The results showed that the decrease of the water contact angle and the increase of the pure water flux for the modified PVDF membrane indicate the improvement of the surface hydrophilicity and protein antifouling.

Besides ATRP and RATRP, another “living”/controlled polymerisation method, which is reversible addition-fragmentation chain transfer polymerisation (RAFT), can also be employed to graft hydrophilic polymer brushes onto the PVDF membrane surface. The PVDF membrane was firstly functionalised by hydroxyl groups, and then 4,4'-Azobis(4-cyanopentanoic acid) (ACP) with azo species reacted with hydroxyl groups to produce the activated PVDF membrane, which was subsequently grafted by MMA or PEGMA with the aid of chain transfer agent (CTA) via RAFT. The modified membrane can further be grafted by 2-(dimethylamino)ethyl methacrylate (DMAEMA) to produce diblock copolymer brushes on the PVDF membrane surface [163].

Although the different “living”/controlled methods have been employed to graft hydrophilic polymer on the PVDF membrane to improve the hydrophilicity and fouling resistance to proteins, most of them also experienced the flux reduction due to the pore plugging, which is inevitable for all surface grafting methods. As a result, blending method was introduced by using hydrophilic polymers, amphiphilic copolymers, and inorganic particles as membrane additives. All other properties of the modified membrane are listed in Table 8.

4.2. Blending modification of PVDF membrane

Blending modification is the most practical way which can be applied to an industrial scale production. The hydrophilic PVDF membrane with other desirable properties can be obtained simultaneously during the membrane preparation process without any pre-treatment or post-treatment procedures, which is usually adopted in surface coating or surface grafting techniques. More importantly, most of the surface grafting techniques focused on the flat sheet membranes, which limited its application in the modification of hollow fibre membranes; while blending some additives with PVDF and subsequent spinning hollow fibre would integrate both phase inversion preparation and hydrophilic modification procedure together using a single-step process. So far, three main types of additives were introduced to modify the PVDF porous membrane, which are hydrophilic polymers or pore forming additives, amphiphilic copolymers, and inorganic particles. All the blending modification methods of the PVDF membrane are listed in Table 9 [11,84,121,125,127,129,182–193].

4.2.1. Hydrophilic polymers

Polyvinylpyrrolidone (PVP), polyethylene glycol (PEG) and poly(methyl methacrylate) (PMMA) are three main hydrophilic polymer additives which are mostly used for the blending with PVDF. The main role of PVP or PEG in the modification and preparation process of the PVDF membrane by non-solvent induced phase inversion is more like pore forming agent rather than hydrophilic agents, because these additives are water soluble and can be washed out during membrane preparation and operation processes [11].

Moreover, the addition of these additives is able to adjust the thermodynamics and kinetics in casting or spinning solution to control the morphology, pore size and pore size distribution [183]. The hydrophilic properties, as well as fouling resistance, would be

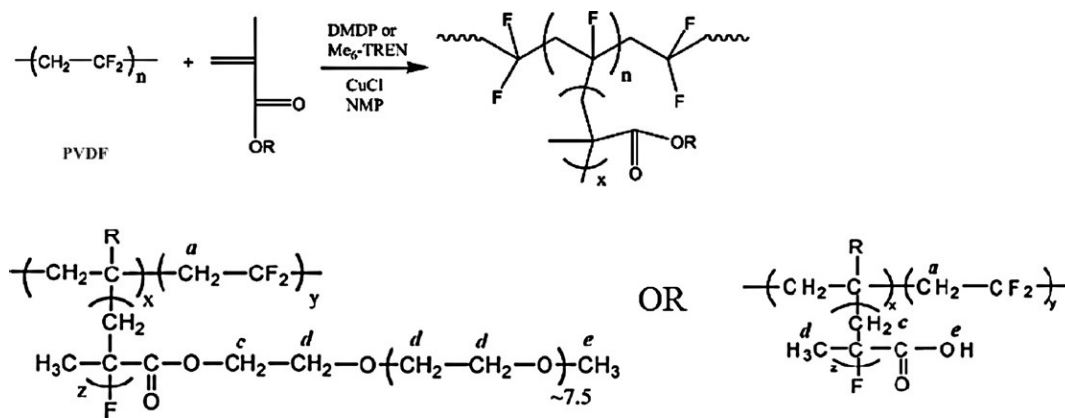


Fig. 6. Schematic synthetic route of amphiphilic copolymer PVDF-g-POEM or PVDF-g-PMAA by ATRP [182].

reduced to some extent as a result of the dissolving out of the hydrophilic polymers due to the incompatibility with PVDF.

However, PMMA provides compatibility with the PVDF matrix and water insolubility [184,194]. Membranes with different hydrophilicity were prepared from blending of PVDF and PMMA. Increasing PMMA content in the blending membrane to 50% delivered a better permeate quality than that of membranes with similar mean pore sizes, indicating that the rejection is affected not only by pore size distribution but also by the solute-membrane interaction. As PVDF concentration is as low as 8.5%, the same to PMMA, the macrovoids appeared below the selective surface, causing a collapse of membrane structure due to the compaction during the filtration process, resulting in a lower value of permeability. Other hydrophilic polymers which are used to study their modification effects on the PVDF porous membrane include sulfonated polycarbonate (SPC) [195], perfluorosulfonic acid (PFSA) [196], and sulfonated polystyrene [197], etc.

4.2.2. Amphiphilic copolymers

Since Mayes et al. preliminarily reported the preparation of protein resistant surfaces on PVDF membrane via surface segregation using the amphiphilic comb-like copolymer P(MMA-r-POEM) as membrane additives in 1999 [198], a great amount of research on the synthesis of amphiphilic copolymers and their applications in the area of hydrophilic and anti-fouling modifications for the PVDF membrane have been investigated. Generally, the synthesis of amphiphilic copolymers can be achieved by general radical polymerisation [186], thermal graft copolymerisation [190], atom transfer radical polymerisation (ATRP) [182] and reversible addition-fragmentation chain transfer polymerisation (RAFT) [189] etc. After polymerisation, the purified amphiphilic copolymer or mixture can be blended with PVDF to obtain a homogenous solution ready to cast or spin. The hydrophilic chains of amphiphilic copolymer would segregate and enrich onto the membrane surface during phase inversion process to minimise the interface free energy. An irreplaceable advantage for the use of amphiphilic copolymer as the membrane additive is its integration of self-organisation modification and phase inversion fabrication of the PVDF membrane. These two objectives can be achieved by one single step process. The hydrophobic backbone chains which are usually composed of PVDF or PMMA guarantee the compatibility with the PVDF bulk while the hydrophilic chains (e.g. PEGMA, PAA) prefer to surface segregate and be self-organised at the water/membrane interface including both membrane surface and pore/channel surface, providing a high coverage of hydrated side chains anchored by a backbone that is insoluble and entangled with the PVDF bulk. Therefore, surface segregation of self-organising amphiphilic copolymers would appear to be a surface modifica-

tion approach capable of simultaneously satisfying all the desired criteria: (a) sufficient coverage of the internal pore channels as well as the selective layer; (b) long-term stability of the modified functionalization; (c) feasibility of the modification approach without any additional processing and low cost; (d) remaining of the bulk membrane properties; (e) simultaneous improvement of permeability and selectivity; (f) diversity of surface engineering.

P(MMA-r-POEM) (P(methyl methacrylate-r-poly(ethylene glycol) methyl ether methacrylate) also expressed as an abbreviation of P(MMA-r-PEGMA)) amphiphilic copolymers were synthesised using less expensive radical polymerisation route [185,186,198]. The methacrylate backbone has a well-known miscibility with PVDF and delivers the long-term stability of amphiphilic copolymers in the membrane matrix. The surface enriched POEM (poly(ethylene glycol) methyl ether methacrylate) chains endow the PVDF membrane with desired hydrophilicity and fouling resistance. The addition of 14.6 vol.% P(MMA-r-POEM) in the bulk membrane exhibited a much higher content of 44 vol.% on the near surface of the flat sheet membrane, contributing a pure water flux of 166.15 L/m² h with the BSA rejection of 20% as listed in Table 9. Furthermore, the modified membrane showed a lower decline trend of BSA solution permeation, indicating a better protein fouling resistance [185]. The hydrophilic PVDF hollow fibre membrane was also fabricated using P(MMA-r-POEM) as the membrane additives [186].

The kinetics investigation of the amphiphilic copolymer during the phase inversion process showed that P(MMA-r-POEM) delayed the onset of demixing and slowed down the precipitation process of PVDF/P(MMA-r-POEM). The hollow fibre showed a pure water flux of 693.0 L/m² h with rejecting carbon ink particles above 128 nm completely. The enhanced hydrophilicity also improved the protein fouling resistance and permeation recovery by simple water washing.

Another amphiphilic copolymer is PVDF based copolymer which is achieved by using PVDF directly as the macro-initiator [182]. The secondary fluorine atoms on the main chain of PVDF backbone can be used to initiate the polymerisation of hydrophilic monomers via ATRP to form comb-like amphiphilic copolymers as shown in Fig. 6. The hydrophilic side chains like POEM or poly(*tert*-butyl methacrylate) grow along the PVDF backbone due to the halogen exchange between fluorine and chlorine in the CuCl catalyst despite the strong C–F binding energy (486 kJ/mol) [182]. Adding 10 wt% PVDF-g-POEM in the bulk PVDF membrane produced a 6.7 wt% content of POEM in the bulk membrane, in the contrast, a 64 wt% content of POEM on the near surface, which are roughly equivalent to that of pure graft copolymer, indicating the surface enrichment of hydrophilic side chains of POEM on the PVDF membrane sur-

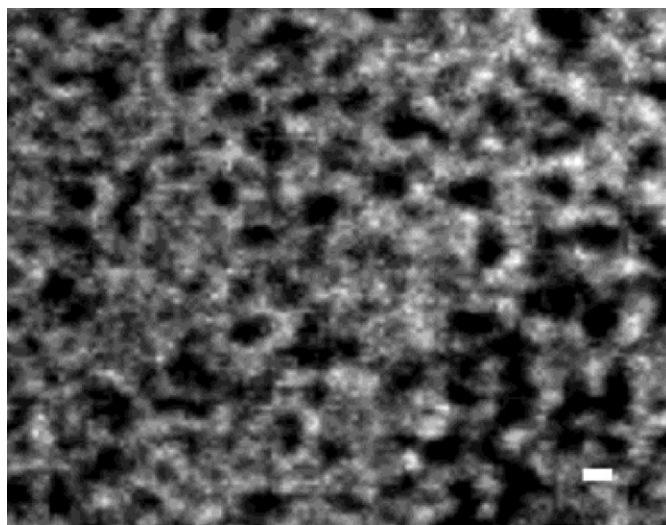


Fig. 7. TEM image of PVDF-g-POEM₉ nanodomain morphology showing interconnected PVDF domains (bright phase), scale bar is 2 nm [199].

face. The contact angle is 53.5° and yields 7 times reduction in BSA adsorption.

PVDF-g-PMAA was also prepared by the grafting copolymerisation of poly(*tert*-butyl methacrylate) on PVDF and subsequent hydrolyzation. The microphase separation as shown in TEM in Fig. 7 [199] and surface segregation provided the membrane with pH-responsive properties. The pure water flux varied from 507 at pH 2 to 29.0 L/m² h at pH 8 due to the corresponding conformation changes of PMAA brushes [187]. Fluorescence microscopy shown in Fig. 8 revealed that surface self-organisation occurred in internal channels throughout the membrane cross-section, as well as the selective surface.

Kang's group synthesised a series of amphiphilic copolymers based on PVDF using ozone pre-treating and subsequent RAFT or thermal graft copolymerisation, and then explored their applications in microfiltration and environmentally stimulated membranes. PVDF was pre-activated by ozone to generate peroxides or hydroxides and then was grafted by PEGMA via RAFT using 1-phenylethyl dithiobenzoate (PDB) as the chain transfer agent

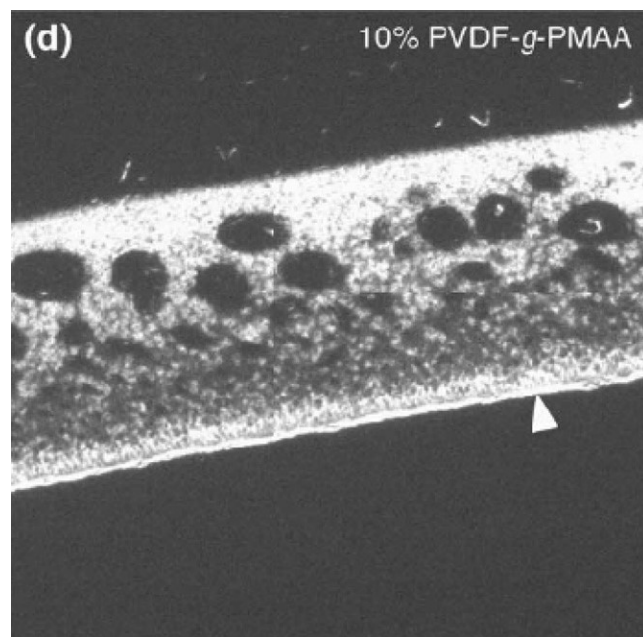


Fig. 8. Fluorescence micrographs of acridine orange (AO) stained membranes [187].

(CTA) [189] as shown in Fig. 9. The synthesised amphiphilic copolymer PVDF-g-POEM has the similar chemical structure, molecular weight, micro-phase separation and surface segregation properties, compared to that of PVDF-g-POEM synthesised by ATRP [182]. Microfiltration membranes fabricated from the PVDF-g-PEGMA comb copolymers by phase inversion exhibited a more uniform pore size distribution, better hydrophilicity and substantial resistance to γ -globulin fouling. PVDF-g-PAAC was also synthesised using the same route as above and then converted into pH-sensitive microfiltration with surface-tethered PAAC chains, which can be furthermore functionalised via surface initiated block copolymerisation with N-isopropylacrylamide (NIPAAm) to obtain the PVDF-g-PAAC-b-PNIPAAm microfiltration membranes exhibiting both pH- and temperature-dependent permeability to aqueous media.

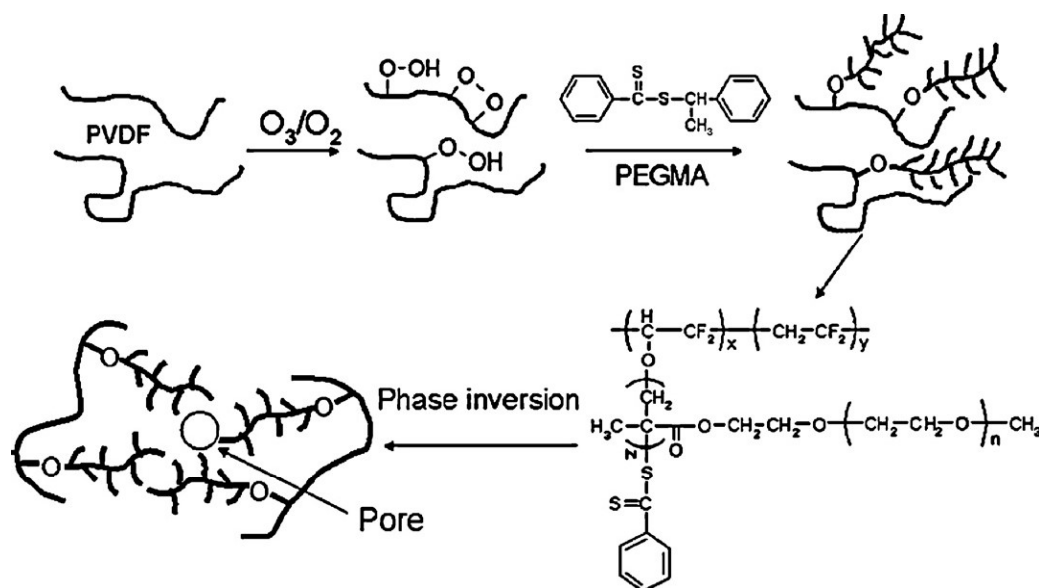


Fig. 9. Schematic synthetic route of amphiphilic copolymer PVDF-g-PEGMA by RAFT [189].

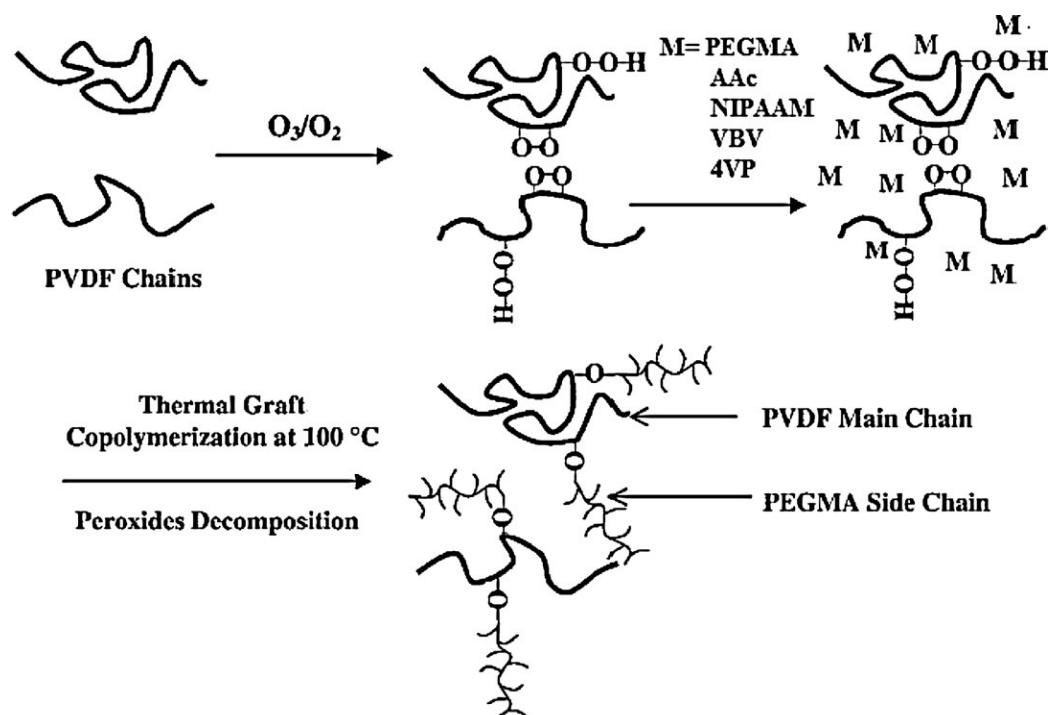


Fig. 10. Schematic synthetic route of amphiphilic copolymer PVDF-g-PEGMA, PVDF-g-PAAc, PVDF-g-NIPAAm, PVDF-g-VBV, and PVDF-g-4VP by thermal graft copolymerisation (TGC) [190,200–203].

Different from Mayes's work using PVDF graft amphiphilic copolymers as the membrane additives, Kang's group used amphiphilic copolymers as the bulk materials to prepare multi-functional micro-porous membranes directly. Other amphiphilic copolymers based on the PVDF backbone were synthesised through thermal graft copolymerisation. PVDF was first pre-treated with ozone and the activated PVDF was then subjected to thermal copolymerisation with the functional monomer e.g. PEGMA [190], AAc and 4VP [200,201], NIPAAm [202], and VBv [203]. The synthetic route is shown in Fig. 10. The microporous membrane fabricated from the corresponding copolymer by phase inversion showed anti-fouling, pH-responsive, temperature-responsive and redox-responsive permeability.

The topological structure (e.g. linear, comb-like, and hyperbranched-star) has an important effect on the properties of amphiphilic copolymers, as well as that of membranes. Amphiphilic hyperbranched-star copolymers (HPE-g-MPEG), which possess a highly branched structure and a large number of terminal functional groups have been synthesised by grafting methoxy poly(ethylene glycol) (MPEG) to a commercially available hydroxyl-terminated aliphatic hyperbranched polyester (HPE) as shown in Fig. 11 [191]. The amphiphilic copolymer (HPE-g-MPEG) was blended with PVDF as the membrane additives to fabricate hydrophilic and the fouling resistant PVDF membrane via

immersion precipitation phase inversion technique. The addition of 3% HPE-g-MPEG imparted the PVDF membrane with a low contact angle of 49° and a high pure water flux of 600 L/m² h. The hydrophilic PVDF membrane also exhibited an enhanced fouling resistance to protein, which possessed an 85% recovery of flux after water washing due to the extraordinary large excluded volume, unique coordination capability with surrounding water molecules of hydrated PEG branched chains [191]. It was found that the MPEG arms in hyperbranched-star polymer can enrich at the membrane surfaces and endow the membranes with improved hydrophilicity, less protein adsorption and filtration performance with increasing MPEG arm length [204].

4.2.3. Inorganic nanoparticles

In the field of blending modification to improve the PVDF porous membrane performance in terms of hydrophilicity, fouling resistance, permeability etc., the incorporation of inorganic nanoparticles has been extensively studied because of its simplicity. It is well known that nanoparticles have unique electronic, magnetic, optical, thermal and mechanical stable properties to improve the performances of membranes to a certain extent due to their small sizes between a few and a few tens of nanometers, large surface areas and strong activities. In comparison to surface coating, surface grafting and blending with polymers, blending with

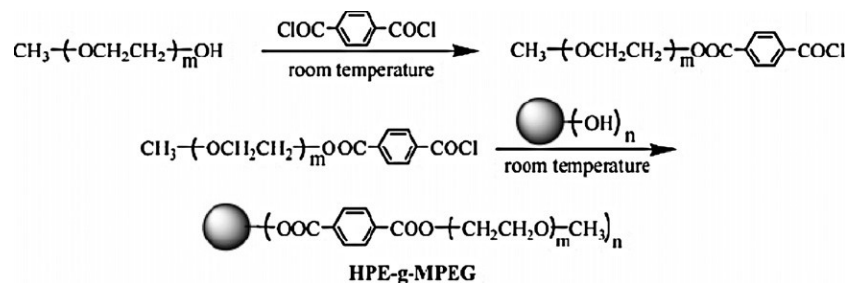


Fig. 11. Synthetic route schematic of amphiphilic copolymer HPE-g-MPEG [191].

inorganic nanoparticles finds its way to enhance the mechanical strength of PVDF membranes to some extent as highlighted in Section 3.2. The uniform dispersion of nanoparticles in the matrix is the crucial process for the preparation of organic–inorganic hybrid membranes. The nanoparticles incorporated into the PVDF membrane mainly include TiO_2 [125,129,192], SiO_2 [130], Al_2O_3 [193] and ZrO_2 [122], etc. so far.

Hydrophilic nanoparticles can be entrapped inside the PVDF ultrafiltration membrane by the addition of TiO_2 to treat activated sludge filtration as membrane bioreactors (MBRs). TiO_2 entrapped membrane showed lower flux decline and greater fouling mitigation because of the enhancement of hydrophilicity. However, the entrapped nanoparticles have a possibility to plug the pores inside; therefore, the deposition or self-assembly of the nanoparticles TiO_2 on the PVDF membrane surface was investigated [125,192]. The results revealed that TiO_2 deposited membrane showed greater fouling mitigation effect compared to TiO_2 entrapped membrane, since large amounts of nanoparticle could be located on membrane surface. TiO_2 was able to self-assemble on poly(vinylidene fluoride)/poly(styrene-alt-maleic anhydride) (PVDF/SMA) blend membrane surface because of the hydrogen bonding interaction between carbonyl of SMA and surface hydroxyl group of TiO_2 . The self-assembly PVDF membrane exhibits extraordinary hydrophilicity, superior permeability and excellent fouling resistance in contrast with PVDF/SMA blend membrane. PVDF/ SiO_2 hybrid hollow fibre ultrafiltration membranes were prepared by the combination of a tetraethoxysilane (TEOS) sol–gel process with a wet spinning method. The addition of SiO_2 into PVDF changes the finger-like pores to sponge-like pores and PVDF crystal formation during the phase inversion process from α crystal phase to β phase. The lowest contact angle was also obtained with 3 wt% TEOS and it increased when TEOS concentration was higher than 3 wt%. The formation of large scale SiO_2 network at higher content of TEOS consumed hydroxyl groups due to the condensation reaction between Si-OH . While SiO_2 could be dispersed finely as smaller particles in the PVDF matrix at lower TEOS concentration and increased the amount of $-\text{OH}$ groups. 3 wt% content of TEOS in the matrix increased the break strength from 1.61 MPa to 2.39 MPa, while decreasing the elongation at break from 257% to 160% [127]. Further addition of TEOS concentration increased the rigidity of membrane and confined the crystallization, which finally led to the decrease of the mechanical strength, so does the elongation at break. Similar results were obtained in the case of the addition of nano-sized Al_2O_3 in the PVDF membrane [121,193]. The optimum amount of nano-sized Al_2O_3 2% by weight was used to acquire the better mechanical and thermal properties as well as the hydrophilicity, permeability and fouling resistance.

Regarding the surface modification, although a large amount of scientific papers have been published, only little information was available in the literature for the application of surface modification by major membrane manufacturers in the world. Millipore corporation presents a variety of ways to produce PVDF hydrophilic membranes by polymerisation of a hydrophilic monomer (e.g. N-vinyl pyrrolidone) in PVDF solution, subsequently casting a membrane from the solution, and then annealing to produce a hydrophilic PVDF membrane [205]. Asahi Kasei Medical Corporation invented a method to improve the hydrophilicity of PVDF membranes. The hydrophobic PVDF membrane was firstly produced by the thermally induced phase separation technique, and then hydrophilic monomer hydroxypropyl acrylate was grafted to PVDF membrane by means of γ -ray irradiation [206]. Siemens Water Technologies Corporation utilised a coating method to modify PVDF membranes by incorporating poly(vinyl methyl ether) (PVME). The PVME can be incorporated either by means of post-treatment, such as by soaking PVDF hollow fibre membranes in a solution of PVME, or by incorporating PVME into the dope solution

for forming the membrane. Therefore, PVME may be cross-linked as a coating on the membrane or dispersed throughout the membrane or both [207].

5. Conclusions

In this review, the latest progress in the production and hydrophilic modifications of PVDF membranes was comprehensively reviewed. At first, the analysis of properties and performances of PVDF as a membrane material such as crystallisation, thermal stability and chemical resistance was focused. And then, more detailed discussions were emphasized on membrane fabrication methods and the related work on modifications for improving fouling resistance properties.

In terms of the PVDF crystallisation during membrane formation, the fabrication condition such as dissolving temperature, precipitation temperature, coagulation medium and coagulation temperature, etc. affected both the degree of crystallisation and crystalline phases. Therefore, crystallisation has a further influence on the final morphology, chemical and thermal stability and mechanical strength of PVDF membranes. It is strongly suggested that further investigations should be conducted about the control of crystallisation (liquid–solid phase separation) on the formation of particular membrane structures such as the bi-continuous pore structure due to the semi-crystalline nature of PVDF.

Regarding the preparation of PVDF membranes, two main methods were so far extensively developed and applied including the immersion precipitation and thermally induced phase separation. However, there is still no consensus on the control of the phase separation mechanism due to the complicated factors during the phase conversion process especially for the fabrication of PVDF hollow fibre membranes. However, the interconnected bi-continuous structure rather than finger like pores for micro- or ultra-filtration membranes seems to prevail due to the obvious enhancement in permeation flux and mechanical strength. Different methods such as vapour induced phase separation or a combination of immersion precipitation and thermally induced phase separation may occupy their unique positions in future.

To improve the fouling resistance of PVDF membranes, various hydrophilic modification techniques can be employed, which is mainly classified into surface modification and blending modification. It is generally understood that the fouling problem of a membrane is caused not only by the hydrophilicity/hydrophobicity, but also by the charge and ionic strength of membranes, morphological properties including surface roughness, pore size distribution, porosity, tortuosity and thickness, the properties of the solutes, the flow mode, membrane module configuration, membrane cleaning, etc. Therefore, system approach should be adapted to combat fouling of membranes in practical processes.

Acknowledgments

The authors gratefully acknowledge the research funding provided by EPSRC in the United Kingdom (Grant No. EP/D068851/1).

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