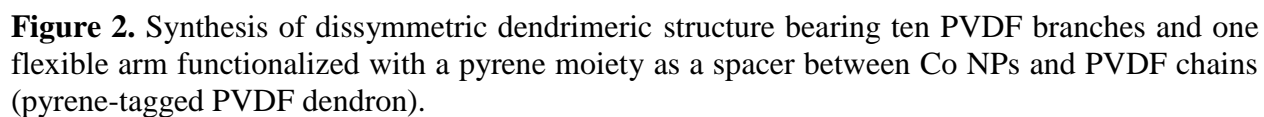
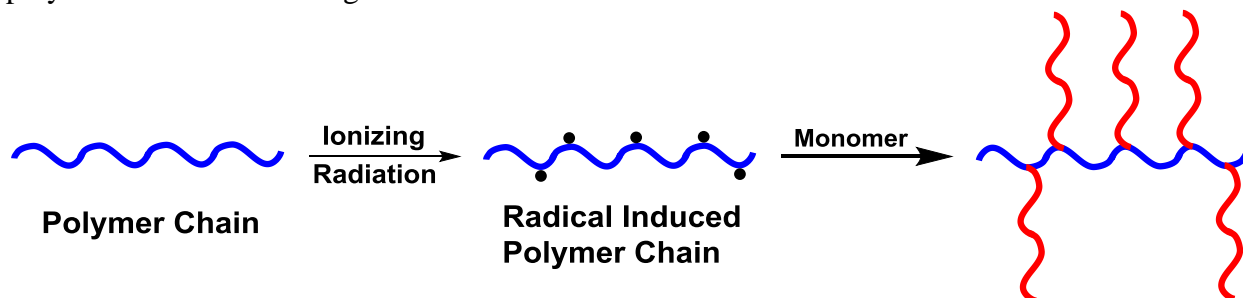


Figure 1. Illustration of various types of complex macromolecular architectures.

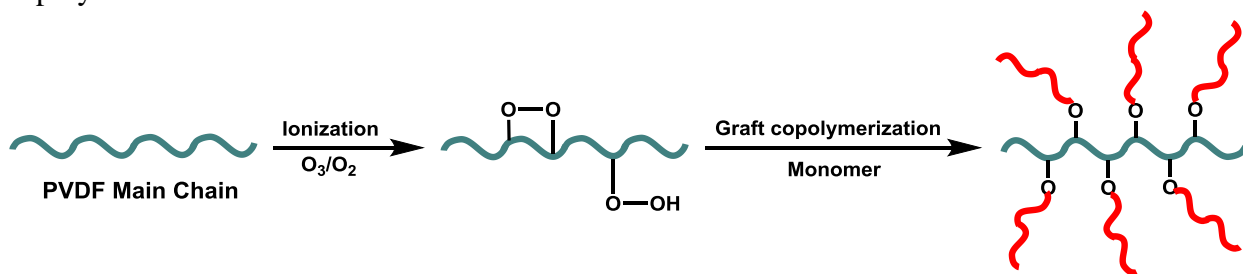


List of Schemes:

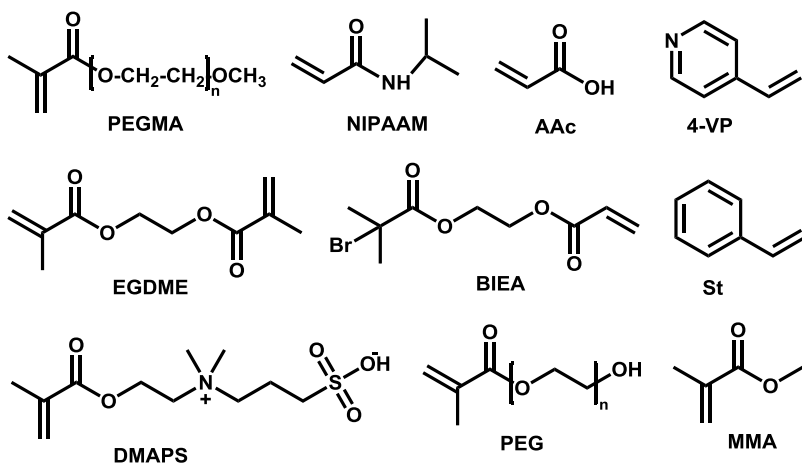
Scheme 1. General scheme of polymer grafting onto PVDF backbone by free radical polymerization *via* ionizing radiation.



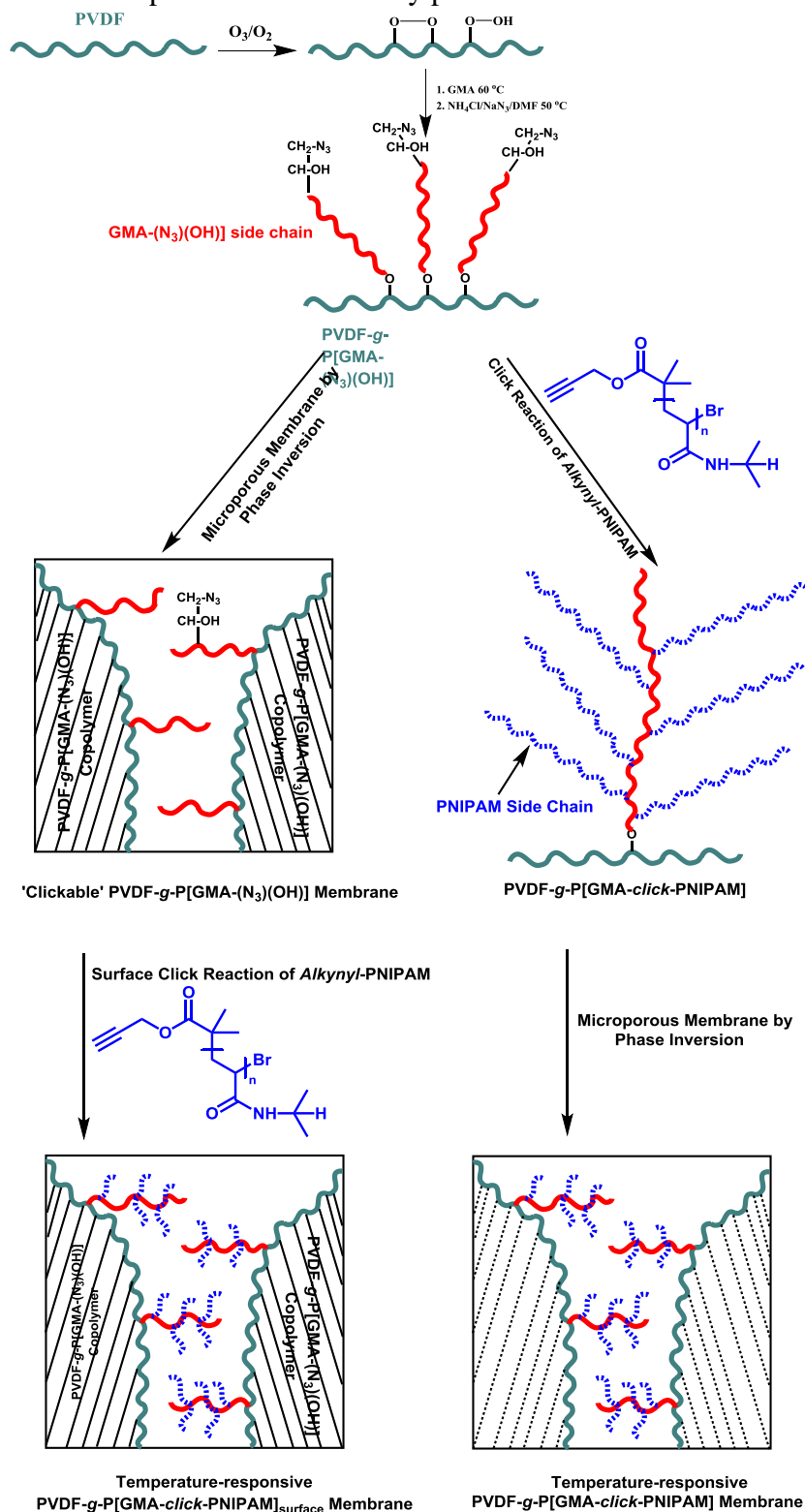
Scheme 2. Schematic illustration for the process of ozone pretreatment and subsequent graft copolymerization of PVDF with various monomers.



Monomers used for grafting copolymerization:



Scheme 3. Synthesis of PVDF-*g*-P[GMA-(N₃)(OH)] graft copolymer and “click” reaction with alkynyl-PNIPAM to produce PVDF-*g*-P[GMA-*click*-PNIPAM] copolymer and subsequently fabrication of the thermoresponsive membrane by phase inversion.



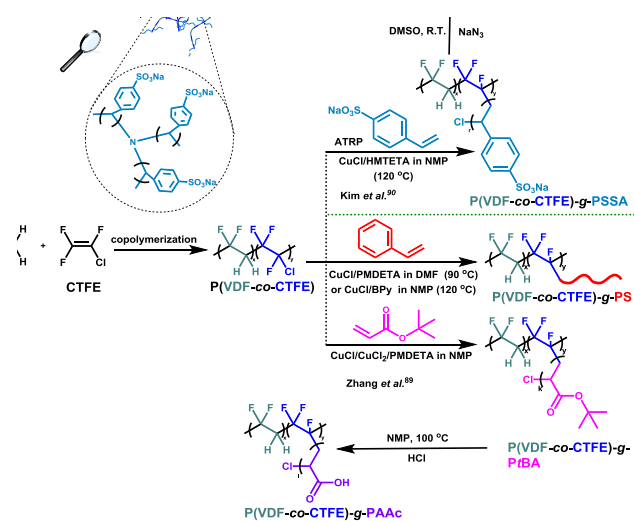
The reaction scheme illustrates the synthesis of PVDF-g-PDA in three main steps:

- Ozonization:** PVDF (polyvinylidene fluoride) is treated with O_3/O_2 to create a hydroperoxide-terminated intermediate.
- Thermally induced radical graft polymerization:** The intermediate reacts with 2,2,2-trifluoroethyl acrylate (a trifluoromethyl-substituted acrylate) to form PVDF-g-PPFA (polyvinylidene fluoride-graft poly(pentafluorophenyl acrylate)).
- Reactive-ester amine reaction:** PVDF-g-PPFA reacts with 4-aminobenzene-1,3-diol ($HCl \cdot H_2N-CH_2-C_6H_3(OH)_2$) to form the final product, PVDF-g-PDA (polyvinylidene fluoride-graft poly(2,4-dihydroxybenzyl acrylate)).

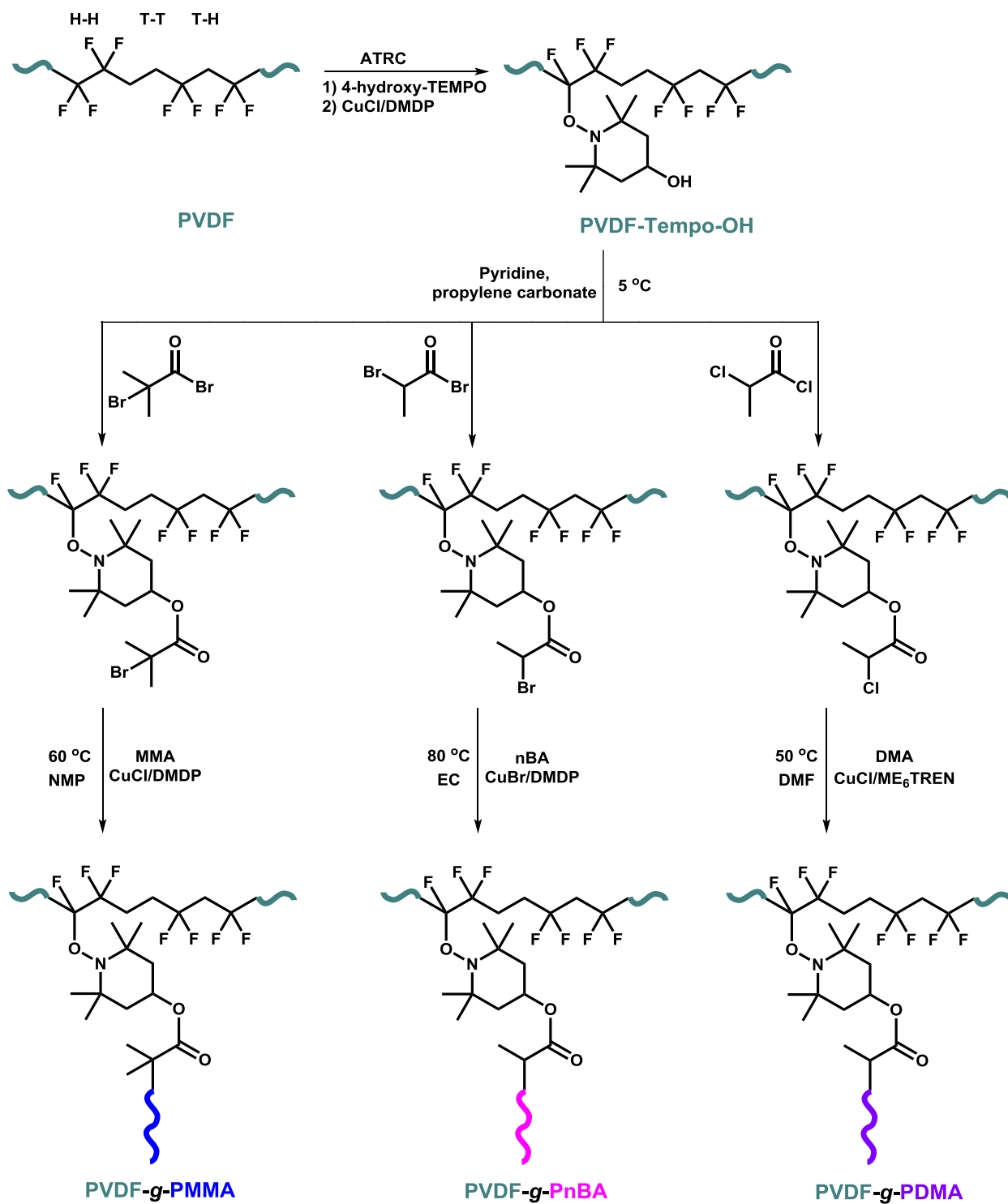
The reaction scheme illustrates the synthesis of PVDF-g-(PVBC-g-PS) and PVDF-g-(PVBC-g-PSSA) through a series of steps:

- PVDF** (polyvinylidene fluoride) is initiated by **EB** (ethylbenzene) to form a macroradical.
- The macroradical is reacted with **PVBC** (polyvinylbenzocyclobutene) in the presence of CuX_2 and 2,2-dipyridyl to form **PVDF-g-PVBC**.
- PVDF-g-PVBC** is reacted with **PS** (polystyrene) in the presence of CuX_2 and 2,2-dipyridyl to form **PVDF-g-(PVBC-g-PS)**.
- PVDF-g-(PVBC-g-PS)** is treated with ClSO_3H and H_2O to form **PVDF-g-(PVBC-g-PSSA)** (polyvinylidene fluoride-g-poly(vinylbenzocyclobutene-co-poly(styrene sulfonic acid))).

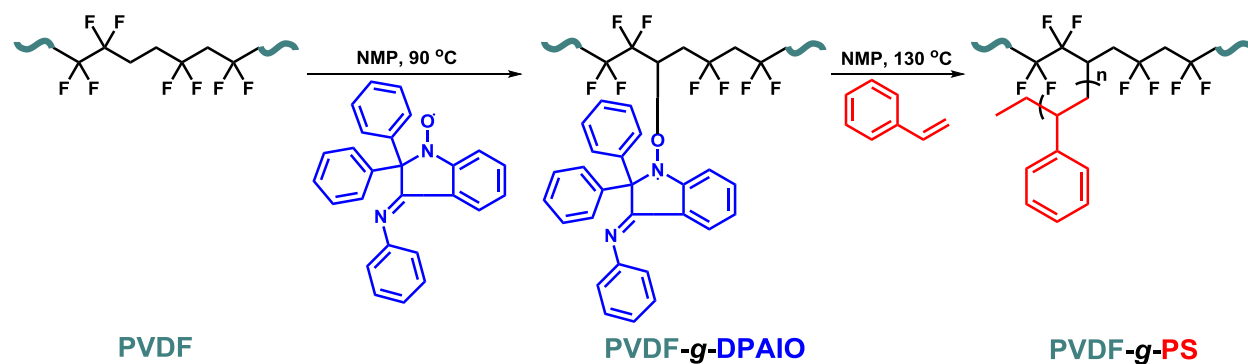
Scheme 7. General synthetic route of poly(VDF-co-CTFE)-*g*-PS or *g*-PAAc or *g*-PSSA by ATRP method.



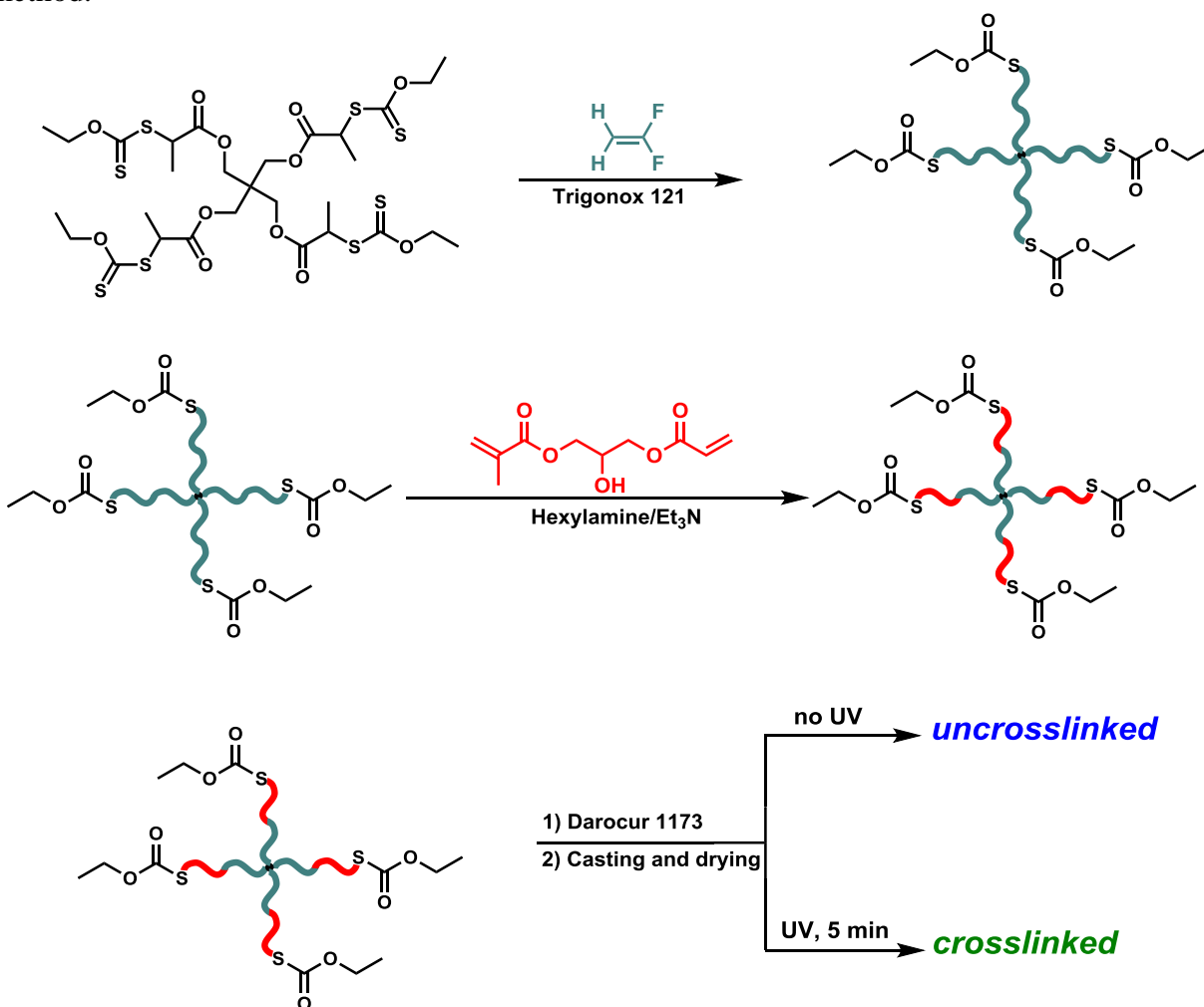
Scheme 8. Synthesis of PVDF-*g*-PMMA or -*Pn*BA or -PDMA graft copolymers by ATRC/ATRP method.



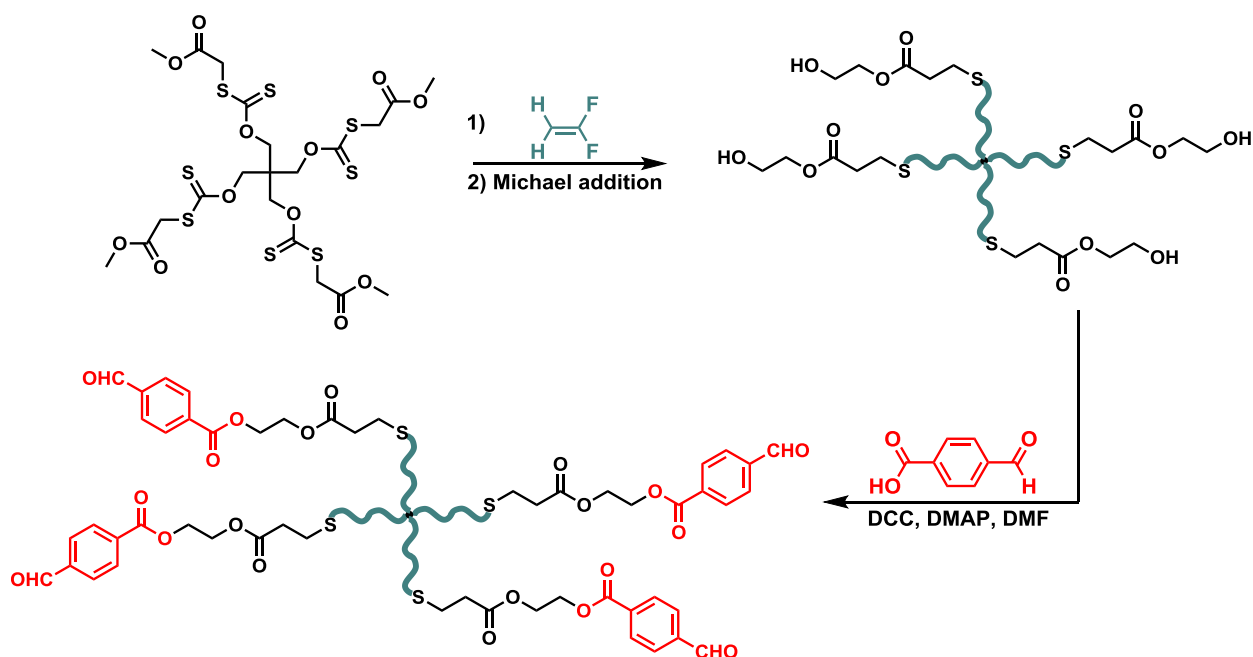
Scheme 9. Synthesis of PVDF-g-PS graft copolymer by nitroxide mediated radical polymerization.



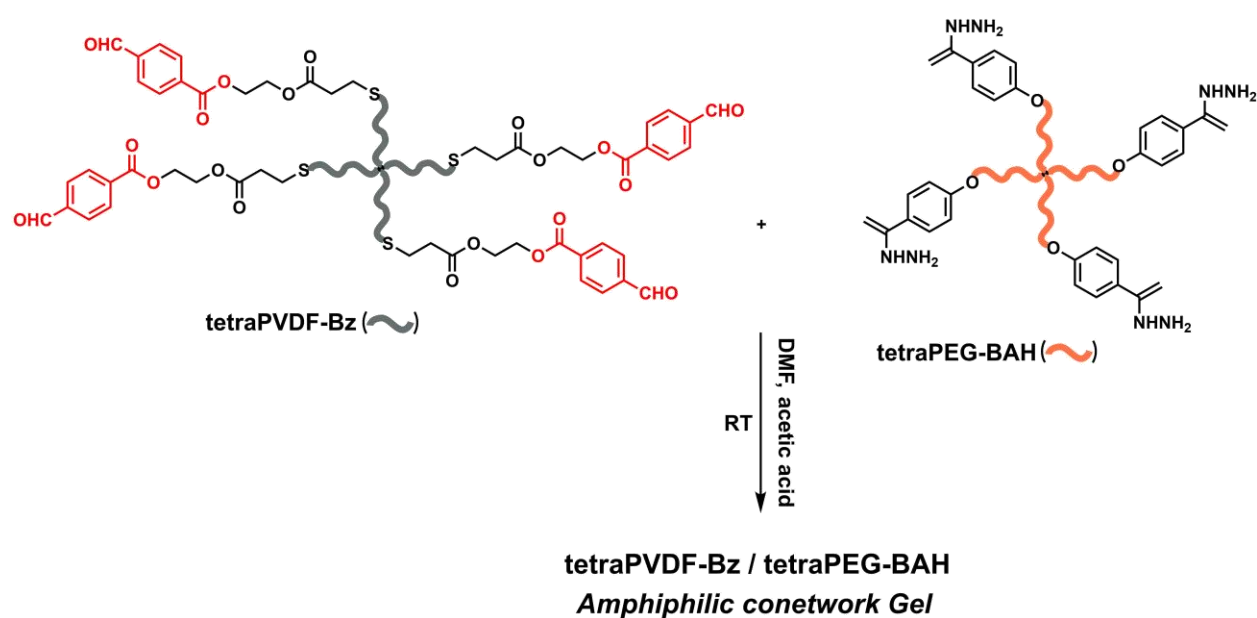
Scheme 10. Synthesis and photocrosslinking of 4-arm star PVDF methacrylate by RAFT method.



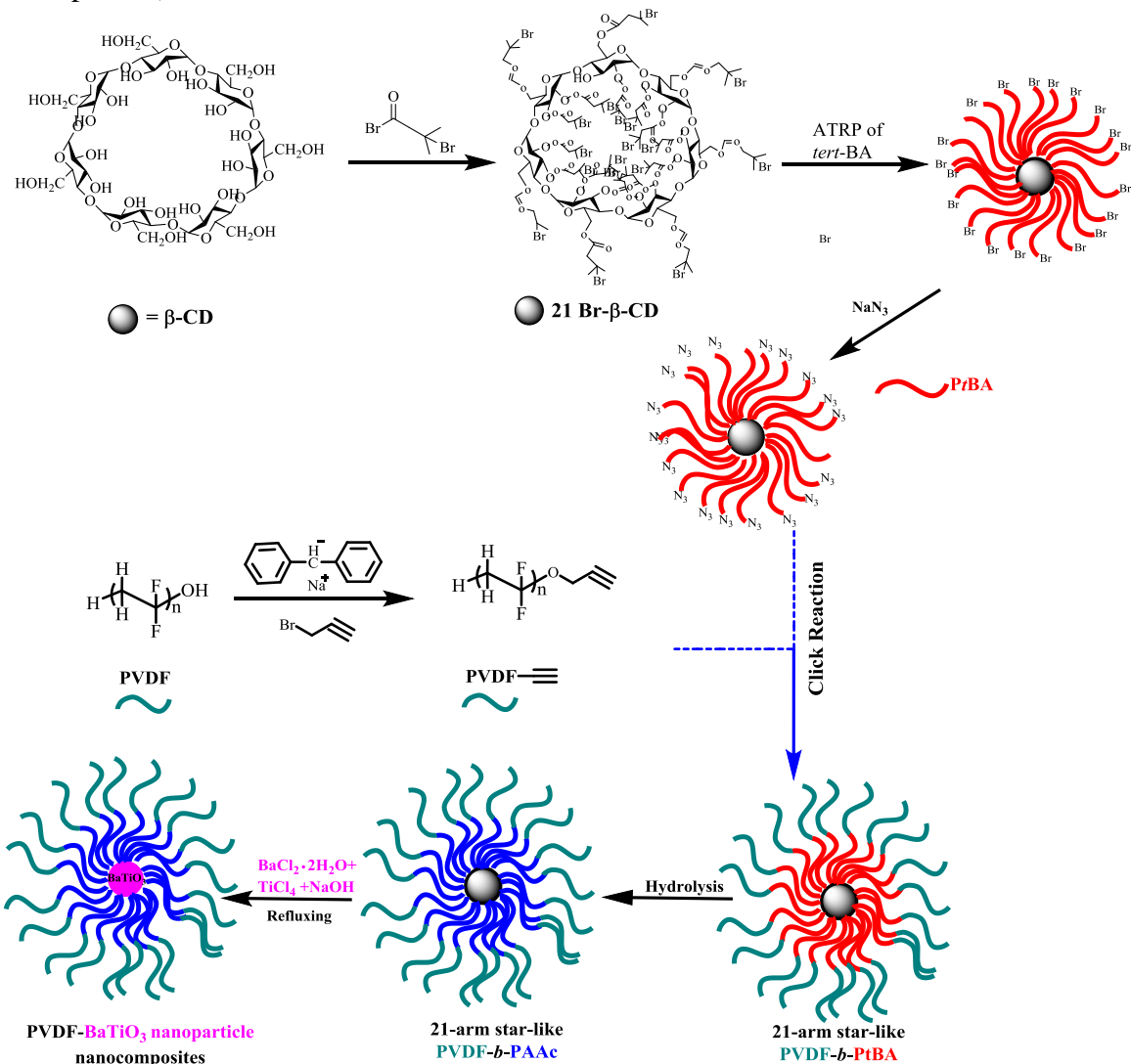
Scheme 11. Chemical reaction between 4-formylbenzoic acid and TetraPVDF-OH (arm degree of polymerization ≈ 34) in order to attach benzaldehyde groups at the termini of the four arms of the hydroxyl end-Functional PVDF star homopolymer.



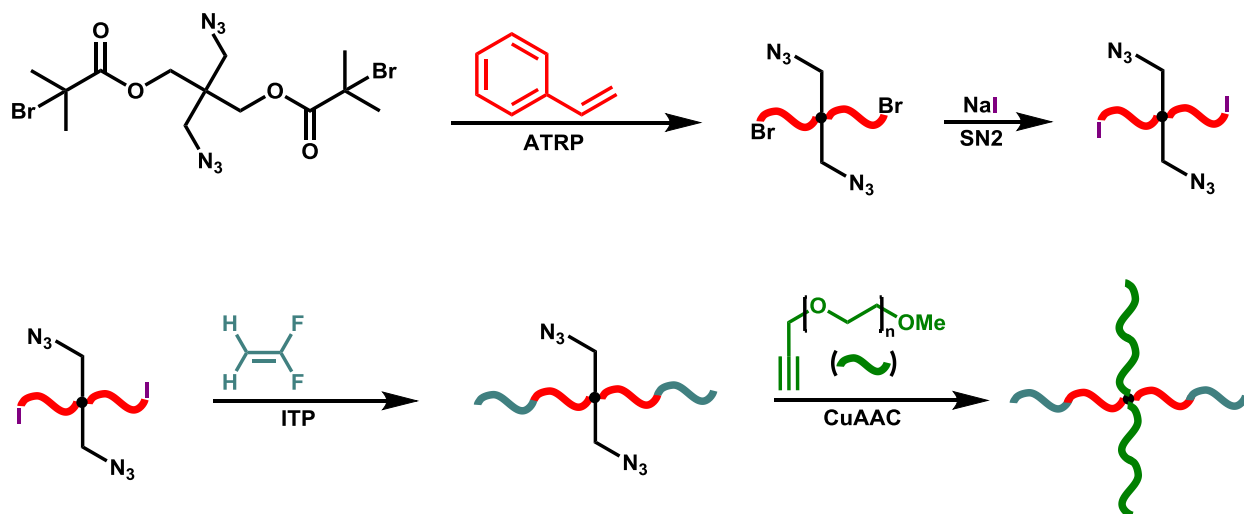
Scheme 12 Condensation reaction between TetraPVDF-Bz and TetraPEG-BAH for the formation of the APCN Gel.



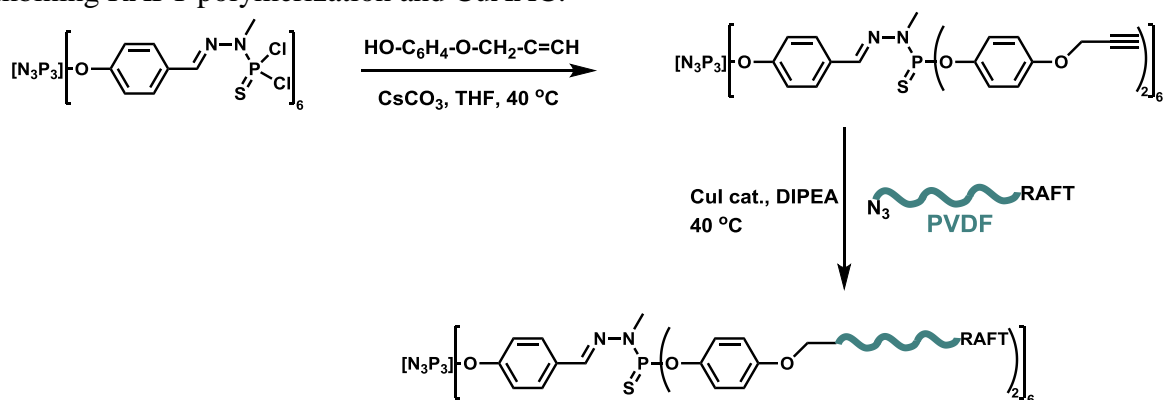
Scheme 13. Synthesis of amphiphilic 21-arm, star-like PAAc-*b*-PVDF diblock copolymer and subsequent conversion into PVDF functionalized BaTiO₃ nanoparticles (PVDF-BaTiO₃ nanocomposites).



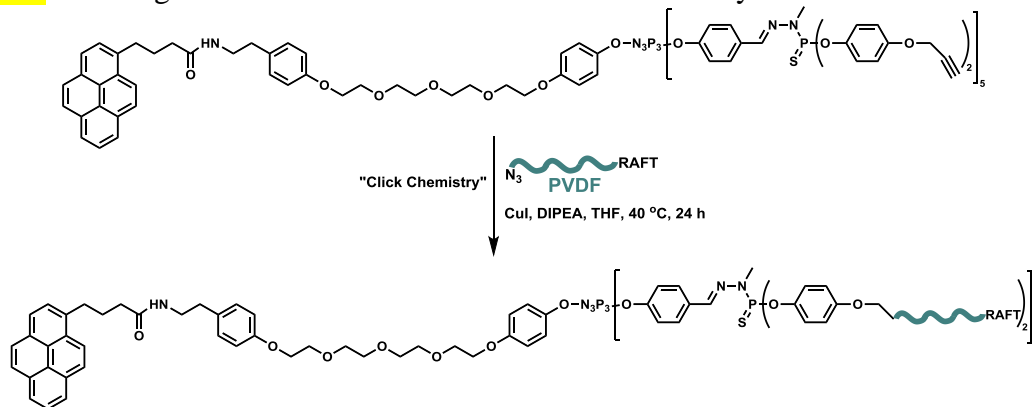
Scheme 14. Synthesis of (PVDF-*b*-PS)₂ (PEG)₂ 4-miktoarm star copolymer by the combination of ATRP, ITP and CuAAC.



Scheme 15. Synthesis of dendritic PVDF with polyphosphorhydrazone, $[P(S)Cl_2]_6$ core by combining RAFT polymerization and CuAAC.



Scheme 16. Grafting of PVDF chains on the dendrimer surface by RAFT and CuAAC.



List of Tables:

Table 1: Overview of the synthesized PVDF-based graft copolymers by conventional radical and controlled radical polymerization methods *with* preirradiation treatment.

Radiation	Method	Initiator or chain transfer	Graft copolymer	References
Electron beam/ozone	Uncontrolled	PVDF-free radicals	PVDF-g-PAAc	[55, 56, 59, 61, 67]
Plasma	Uncontrolled/controlled	PVDF-free radicals/ATRP	PVDF-g-PMAA	[83, 97]/[108]
Electron beam	uncontrolled	PVDF-free radicals	PVDF-g-PSSA	[83, 91, 92]
γ ray	uncontrolled	PVDF-free radicals	PVDF-g-PHEA	[93]
Ozone	uncontrolled	PVDF-free radicals	PVDF-g-PMMA	[59]
Ozone	uncontrolled	PVDF-free radicals	PVDF-g-PGMA	[59]
Ozone	uncontrolled	PVDF-free radicals	PVDF-g-P(PEGMA)	[64, 65, 94]
Ozone	uncontrolled	PVDF-free radicals	PVDF-g-PNIPAM	[62]
Ozone	uncontrolled	PVDF-free radicals	PVDF-g-PDMAPS	[70]
Ozone	uncontrolled	PVDF-free radicals	PVDF-g-PS	[59]
Ozone	uncontrolled	PVDF-free radicals	PVDF-g-P2VP	[67]
Ozone	uncontrolled	PVDF-g-P[GMA(N ₃)(OH)]	PVDF-g-P[GMA- <i>click</i> -PNIPAM]	[71]
Ozone	uncontrolled	PVDF-g-PPMA	PVDF-g-[PMA- <i>click</i> -MPS]	[72]
Ozone	uncontrolled	PVDF-g-PDA	PVDF-g-PDA/PNIPAM (or PEG or HPG)	[73]
Plasma	uncontrolled	PVDF-free radicals	PVDF-g-P(PEGMA)	[94]
Electron beam	NMP	PVDF-TEMPO capped	PVDF-g-PSSA	[82]
Electron beam/γ-rays	ATRP/uncontrolled	PVDF-g-PVBC	PVDF-g-PVBC-g-PS	[80, 81]
Ozone	ATRP	PVDF-g-PBIEA	PVDF-g-PBIEA- <i>ar</i> -NaPSS	[68]
Ozone	ATRP	PVDF-g-PBIEA	PVDF-g-PBIEA- <i>ar</i> -PDMAEMA	[69]
Ozone	RAFT	PVDF-dithioester group	PVDF-g-PEGMA	[74]
Ozone	RAFT	PVDF-dithioester group	PVDF-g-PAAc- <i>b</i> -PNIPAM	[75]
Ozone	RAFT	PVDF-azide group	PVDF-g-PMMA- <i>b</i> -PDMAEMA	[96]
			PVDF-g-PPEGMA- <i>b</i> -PDMAEMA	

Table 2: Overview for the synthesis of PVDF-based graft copolymers from controlled radical polymerization methods without preirradiation treatment.

Method	Initiator or chain transfer	Graft copolymer	References
Free radicals/ATRP	PVDF	PVDF- <i>g</i> -PEGMA	[99]/ [91, 92, 94, 97, 98, 100, 101]
ATRP	PVDF	PVDF- <i>g</i> -PMMA	[92]
ATRP	PVDF	PVDF- <i>g</i> -PtBA	[107]
ATRP	PVDF	PVDF- <i>g</i> -PnBMA	[95]
ATRP	PVDF	PVDF- <i>g</i> -PDMAEMA	[94, 95]
ATRP	PVDF	PVDF- <i>g</i> -PSPMA	[93]
ATRP	PVDF	PVDF- <i>g</i> -PNIPAAm	[102-104]
ATRP	PVDF- <i>co</i> -PBDFO	PVDF- <i>g</i> -PS	[111]
ATRP/uncontrolled	PVDF	PVDF- <i>g</i> -PSSA	[84,108]
ATRP	PVDF	PVDF- <i>g</i> -SPS	[145]
ATRP	PVDF	PVDF- <i>g</i> -PGMA- <i>g</i> -PGHT	[106]
NMP	PVDF- <i>g</i> -DPAIO	PVDF- <i>g</i> -PS	[114]
uncontrolled	PVDF-free radicals	PVDF- <i>g</i> -PS	[111]
uncontrolled	PVDF-free radicals	PVDF- <i>g</i> -PMABS	[85]