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Sanjib Banerjee, Arindam Chakrabarty, Nikhil Singha, Bruno Ameduri. Recent advances in the reversible deactivation radical (co)polymerization of fluorinated alkenes/acrylates/methacrylates/styrenes. Nikhil K. Singha; Jimmy Mays. Reversible Deactivation Radical Polymerization. Synthesis and Applications of Functional Polymers, De Gruyter, pp.183-220, 2019, 9783110639995. 10.1515/9783110643695-006 . hal-03149334

HAL Id: hal-03149334

<https://hal.science/hal-03149334>

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6 Recent Advances in the Reversible Deactivation Radical (Co)Polymerisation of Fluorinated Alkenes/Acrylates/Methacrylates/Styrenes

Sanjib Banerjee, Arindam Chakrabarty, Nikhil K. Singha and Bruno Ameduri

6.1 Introduction

Due to their i) unique combination of extraordinary physical properties originating from their low polarisability, strong electronegativity, small van der Waals radius of the F atom (1.32 Å) and strong C–F bond (bond energy dissociation = 485 kJ mol⁻¹) and ii) great diversity of morphologies, ranging from semicrystalline to a completely amorphous structure to thermoplastic elastomers (TPE), fluorinated (co)polymers have emerged as remarkable speciality macromolecules [1–5]. Hence, fluoropolymers bearing highly F-rich backbones exhibit excellent thermal, chemical and ageing/weather resistance, as well as high inertness to solvents and acids, and low flammability/refractive index/dielectric constants/moisture absorption. Polymers bearing a dangling perfluorinated groups are highly repellent towards oil, soils and water. Furthermore, the presence of strong C–F bonds in fluoropolymers improves resistance to oxidative and hydrolytic degradation, and imparts low surface energy.

Due to the exceptional properties of fluoropolymers described above, these speciality macromolecules have been extensively used in many high-tech applications, such as in the automobile industry (~300 g of fluoropolymers per car) [5], in components of fuel cells and lithium-ion batteries, in aerospace and aeronautics (as seals/gaskets/O-rings for use at extreme temperatures for tanks of liquid hydrogen or hydrazine in boosters of space shuttles [5, 6]), in the petrochemical industry (pipes and coatings as liners), microelectronics, chemical engineering (for the production of high-performance membranes [7]), textile treatment, building ultraviolet (UV)-resistant paints and coatings and for graffiti and stone protection, mainly as coating materials for protecting old heritage monuments [8], and for producing waveguides, cores and claddings of optical fibres [9]. In spite of their high production cost (arising from the small scale fabrication, the production/purification of the gaseous monomers, requirement for unique polymerisation processes/instrumental set-up), extensive

academic/industrial research is currently focused on developing technologies involving fluoropolymers.

The journey of fluoropolymers began with the accidental discovery of polytetrafluoroethylene (PTFE) in 1938 by the DuPont Company, prepared *via* the free radical polymerisation (FRP) of tetrafluoroethylene (TFE) [10]. PTFE gained immediate recognition as an efficient coating material due its excellent hydrophobicity, oleophobicity, anti-sticking and thermal properties. Since then, the development of new fluorinated polymers has attracted research interest in industry as well as in academia. In spite of their immense potential in high-value applications, fluoropolymers suffer from two main limitations: i) poor solubility in common organic solvents arising from their high crystallinity (especially of homopolymers, PTFE is 95% crystalline) and ii) difficulty in curing or crosslinking [11]. To overcome these limitations, extensive research was carried out in the 1950s and 1960s to develop a new generation of fluorinated macromolecules [4, 5, 11–13] containing comonomers bearing bulky pendant groups. These groups induce a certain degree of disorder in the macromolecule to suppress the high crystallinity of the fluorinated homopolymers and thus enhance their solubility in organic solvents. By fine-tuning the choice of the comonomer, fluorinated copolymers with exciting properties can be prepared to realise high-value applications in specific areas.

FRP methods are generally employed for the synthesis of fluoropolymers based on fluorinated monomers [1–6]. However, FRP techniques suffer from certain limitations by producing polymers with uncontrolled molecular weight (MW), broad dispersity ($\bar{D}$), gel fraction and so on. In contrast, the development of reversible deactivation radical polymerisation (RDRP) techniques allows the limitations of FRP to be overcome. However, few strategies of RDRP have been developed for the polymerisation of fluorinated monomers in order to prepare fluorinated homopolymers, random copolymers and block copolymers, as reviewed in a recent article [14]. Additionally, RDRP techniques offer the scope to modify various substrates *via* surface-initiated controlled polymerisation. This provides the opportunity to introduce fluoropolymers to improve the water and oil repellency in a substrate. Due to the presence of highly-electronegative fluorine atoms, fluoromonomers display certain differences in reactivity compared to hydrocarbon monomers. Moreover, the incompatibility between a fluoropolymer and its hydrocarbon analogues leads to the self-stratification of fluoropolymer segments. Thus, a polymer composed of a fluoropolymer and its hydrocarbon analogue displays enrichment of the fluoropolymer phase at the surface compared with the bulk. This phenomenon has led researchers to prepare fluorinated random/block copolymers with low fluoropolymer content.

RDRP has undergone continuous development to become a precision technique yielding polymers bearing predesigned end-groups with precisely controlled molar

masses, narrow $\bar{M}$ and well-defined architectures (telechelic, block, graft or star copolymers) [15]. The exceptional and inventive development of modern RDRP techniques has been discussed in detail in many books and reviews (more than 13,000 papers have been published on RDRP over the last 20 years) [4, 15, 16]. Thus, in this chapter we will discuss these developments briefly and, for further reading, readers may consult the above-mentioned references. RDRP is beginning to translate from academic research labs to industries for the development of adhesives, dispersants, lubricants, high-performance elastomers, for application as novel electrical [17] and biomedical materials [18], in electronics [19], and in aerospace, automotive and medical industries [20, 21].

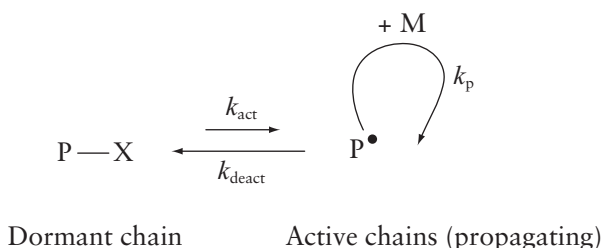
This chapter will first briefly review and highlight fundamental aspects of RDRP for the production of well-defined polymers. Some exciting recent examples of macromolecular architectures prepared by the RDRP of fluorinated alkenes/acrylates/methacrylates/styrenes for designed applications will also be presented, considering the fact that a more exhaustive review on controlled radical (co)polymerisation of fluoroalkenes was published two years ago [22]. We conclude with an outline of future directions for the applications of RDRP of fluorinated alkenes for the synthesis of advanced polymer materials with many high-value applications.

6.2 Fundamentals and Developments of Controlled Radical (Co)Polymerisation

Since the mid-1990s, extensive research has been carried out to develop controlled/living radical polymerisation [15]. The origin of control in the RDRP process arises from the i) nature of the (macro)radicals having very short ‘active’ life times and ii) fast exchange between living ‘active’ macroradicals and dormant chains (**Scheme 6.1**). Both features reduce undesirable chain transfer and terminations.

In his pioneering work, Tatemoto reported iodine transfer (co)polymerisation of fluoroalkenes in 1978 [20, 23]. Subsequently, Otsu and co-workers developed the initiation-transfer-termination method [24], but not using fluorinated monomers. Recently, nitroxide-mediated polymerisation (NMP) [25], atom transfer radical polymerisation (ATRP) [26], reverse iodine transfer polymerisation (RITP) [27], reversible addition-fragmentation chain transfer (RAFT) [28], including macromolecular design *via* interchange of xanthates (MADIX) polymerisation [21, 29], organoheteroatom-mediated radical polymerisation based on tellurium, bismuth, antimony [30] and cobalt-mediated radical polymerisation (CRMP) using *bis*(acetylacetonato)cobalt(II) [Co(acac)₂] [31] were successfully developed as RDRP techniques. Chung and co-workers [32] reported the synthesis of chain end-functionalised fluoropolymers *via* RDRP using functional borane initiators.

Recently, Goto and co-workers [33] developed reversible complexation-mediated RDRP.



Scheme 6.1 Reversible fast exchange between active and dormant species in RDRP

The development of RDRP methods for fluoromonomers has been hindered by the recombination of the growing macroradicals [34]. Thus, various combinations of fluorinated organic compounds have been used as initiators, monomers, chain transfer agents (CTA) or solvents to achieve RDRP of fluoromonomers [35]. Detailed surveys of the development of state-of-the-art strategies for the RDRP of fluorinated monomers are given in two previous reviews [14, 22]. Thus, this section focuses on recent exciting discoveries involving the RDRP of fluoroalkenes, especially iodine transfer polymerisation (ITP) and RAFT/MADIX polymerisation, followed by a second section devoted to the RDRP of fluorinated (meth)acrylates and styrenic monomers.

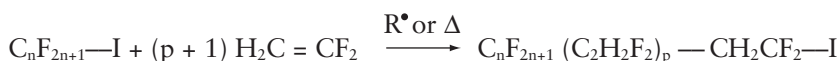
6.3 Controlled Radical Polymerisation of Fluoroalkenes

6.3.1 Iodine Transfer Polymerisation of Fluoroalkenes

6.3.1.1 History and Production of Copolymers Produced by Iodine Transfer Polymerisation

The development of ITP of fluoropolymers was inspired by the radical telomerisation of fluoroalkenes [36], as reviewed previously [4]. In the late 1970s, Tatemoto introduced the clever concept of RDRP as the iodine transfer (co)polymerisation of fluoroalkenes

including vinylidene fluoride (VDF) [23a]. During the ITP of fluoroalkenes, the terminal active bond (pseudo-living centre) of the growing polymer always contains a C–I bond which originates from the iodine-containing CTA and the monomer, as displayed in **Scheme 6.2**. The reactivity of this terminal group always remains the same during the entire duration of the polymerisation, and even after quenching of the polymerisation [13, 37].



Scheme 6.2 ITP of VDF in the presence of 1-iodoperfluoroalkanes as the CTA. Reproduced with permission from B. Ameduri, *Macromolecules*, 2010, **43**, 24, 10163. ©2010, American Chemical Society [14]

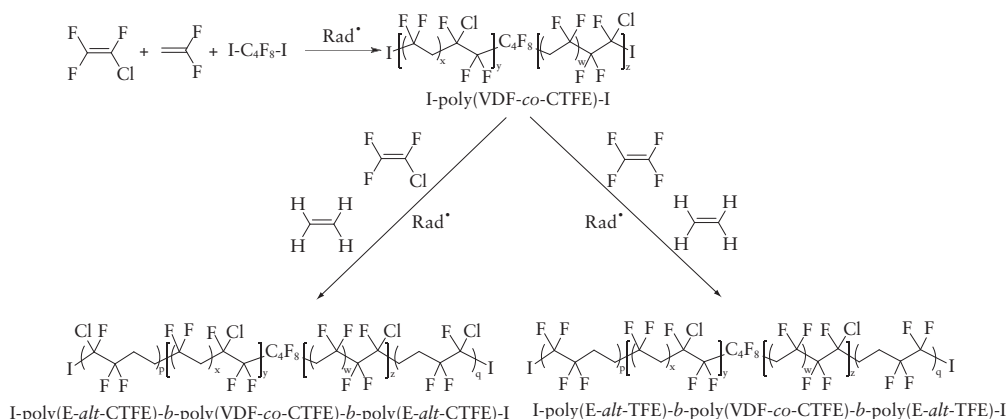
The high transfer rate ($C_{tr} = 7$ at 74 °C [38]), compared with the termination rate, provides control during ITP. Apostolo's group [37] studied the kinetics of the radical copolymerisation of VDF and hexafluoropropylene (HFP) in microemulsion to produce polymers with well-defined microstructure. In ITP, termination occurs exclusively by recombination [34].

Peroxide initiators and perfluorinated or chlorofluorinated solvents originally used by Tatemoto and co-workers [23] were subsequently improved by employing diiodo [23, 39] and polyiodo compounds [23]. Boyer and co-workers studied the ITP of VDF utilising various 1-iodofluoroalkanes as CTA. Among the CTA employed, $\text{C}_6\text{F}_{13}\text{I}$ and $\text{C}_6\text{F}_{13}\text{CH}_2\text{CF}_2\text{I}$ induce a pseudo-living tendency [38], originating from the lability of the $\text{CF}_2\text{—I}$ bond and the fast decomposition of $\text{C}_6\text{F}_{13}\text{I}$, whereas $\text{HCF}_2\text{CF}_2\text{CH}_2\text{I}$ induces uncontrolled ITP ($C_{tr} = 0.7$ at 74–140 °C) [38]. However, in the case of unsymmetrical fluoroolefins (such as VDF), after incorporation of ~12–15 VDF units in the growing polyvinylidene fluoride (PVDF) macroradical, head-to-head chain defects start to become evident. Reactivation from these defective chain ends ($\text{—CF}_2\text{CH}_2\text{—I}$) is not possible, resulting in broader $\bar{D}$.

Beuermann's group developed the ITP of fluoromonomers in supercritical carbon dioxide (scCO_2) at 120 °C and 1,500 bar, in a homogeneous phase using $\text{C}_6\text{F}_{13}\text{I}$ [40a] or $\text{IC}_6\text{F}_{12}\text{I}$ [40b] as the CTA, and produced polymers with narrow $\bar{D} = 1.2\text{--}1.5$. The use of scCO_2 in the polymerisation was inspired by DeSimone and co-workers' article [41] which verified that scCO_2 can solubilise fluoropolymers.

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Tatemoto and co-workers [20] also pioneered the synthesis of hard-*b*-soft-*b*-hard triblock copolymers *via* the ITP of VDF and HFP in the presence of an α,ω -diiodoperfluoroalkane ($\text{IC}_4\text{F}_8\text{I}$ or $\text{IC}_6\text{F}_{12}\text{I}$). Subsequent chain extension with VDF (or ethylene and TFE) (Scheme 6.3) yielded TPE with potential application as O-rings, hot melts, pressure-sensitive adhesives, tough transparent films and sealants for high-tech applications in aeronautics or automotive industries. Daikin Company marketed these TPE as early as 1984, under the trademark Dai-el[®]. They are composed of soft segments, e.g., low-glass transition temperature (T_g) blocks, containing the poly(VDF-*co*-HFP) as above or composed of poly[VDF-*co*-chlorotrifluoroethylene (CTFE)], poly(VDF-*ter*-HFP-*ter*-TFE), poly[ethylene-*ter*-perfluoromethyl vinyl ether (PMVE)-*ter*-TFE] elastomeric blocks. Hard blocks are composed of various crystalline polymeric sequences [PVDF in the case of Dai-el[®] T-630 [20, 42], PTFE, or poly(ethylene-*alt*-TFE) or poly(ethylene-*ter*-TFE-*ter*-HFP) hard block in the case of Dai-el[®] T530 thermoplastics] [42]. After a gap of several years, these TPE were also produced by Ausimont (now Solvay Specialty Polymers) and DuPont, under the Tecnoflon[®] and Viton[®] tradenames, respectively.



Scheme 6.3 Synthesis of triblock TPE using telechelic diiodo poly(CTFE-*co*-VDF) copolymers as CTA [42a]. Reproduced with permission from F. Boschet and B. Ameduri, *Chemical Reviews*, 2014, **114**, 2, 927.
©2014, American Chemical Society [42b]

The ITP of VDF and CTFE, first achieved by the Daikin Company [43] in the presence of $\text{IC}_4\text{F}_8\text{I}$ as the CTA, led to I-poly(VDF-*co*-CTFE)-I (Scheme 6.3), where the mol%

of VDF and CTFE were 55 and 45, respectively, as an elastomeric block ($T_g = -7^\circ\text{C}$). This α,ω -bis(iodinated)-functionalised soft segment was able to undergo chain extension with a poly(ethylene-*alt*-CTFE or TFE) to yield hard-soft-hard triblock copolymer TPE for use as artificial lenses [43]. The melting points of the hard blocks containing either poly(ethylene-*alt*-CTFE) or poly(ethylene-*alt*-TFE) copolymers were 247 or 252 $^\circ\text{C}$, respectively (Scheme 6.3).

Mladenov and co-workers reported the synthesis and characterisation of fluorinated copolymers containing VDF and HFP, through the use of 1,6-diiodoperfluorohexane as the CTA *via* an ITP process [44], as well as fluorinated telomers based on VDF using $\text{C}_6\text{F}_{13}\text{I}$ or $\text{C}_4\text{F}_9\text{I}$ [45].

Recently, Asandei and co-workers developed photomediated RDRP and block copolymerisation of VDF and other monomers using different metal carbonyls employing $\text{Mn}_2(\text{CO})_{10}$ as a visible light photocatalyst, in conjunction with iodoperfluoroalkanes (R_fI s) and respective alkyl halides (Table 6.1). The reactions were carried out in sealed glass tubes. Their extensive research established dimethyl carbonate (DMC) as the best solvent under the reaction conditions [46].

Table 6.1 Dependence of M_n and MW/M_n on conversion in $\text{Mn}_2(\text{CO})_{10}$ - photomediated VDF-IDT							
Monomer (M)	PVDFI or I-PVDF-I		$[\text{M}]/[\text{PVDF}]/$ $[\text{Mn}_2(\text{CO})_{10}]$	Conv. (%)	M/VDF	M_n	$\bar{D}$
	M_n	$\bar{D}$					
Styrene	2,500	1.34	60/1/2	67	70/30	14,500	2.25
	11,500	1.48	4,000/1/5	12	92/8	44,700	1.72
Butadiene	1,400	1.48	200/1/1	25	62/38	4,700	2.00
Vinyl chloride	1,800	1.29	100/1/1	35	77/23	20,100	1.52
VAc	1,500	1.49	100/1/0.2	30	35/35	11,000	1.70
Methyl acrylate	2,300	1.52	75/1/4	40	72/28	9,000	2.46
Acrylonitrile	2,100	1.31	50/1/1	25	74/26	25,800	2.33
VAc: Vinyl acetate							
M_n : Number average molecular weight							
Reproduced with permission from A.D. Asandei, O.I. Adebolu and C.P. Simpson, <i>Journal of the American Chemical Society</i> , 2012, 134, 14, 6080. ©2012, American Chemical Society [46]							

They later employed this $\text{Mn}_2(\text{CO})_{10}$ -system to prepare well-defined sulfonated and fluorinated block copolymers for potential application in fuel cell membranes

by sequential copolymerisation of neopentyl styrene sulfonate and VDF [47]. Subsequently, they employed hypervalent iodide carboxylate, $(\text{CX}_3\text{CO}_2)_2\text{I}^{\text{III}}\text{Ph}$, to develop a metal-free protocol in conjunction with external $[\text{I}(\text{CF}_2)_6\text{I}]$ and *in situ* generated (CF_3I) iodinated CTA to achieve the RDRP of VDF and to produce poly(VDF)-*b*-poly(M) block copolymers [48] [where ‘M’ stands for styrene (S), butadiene, 2,2,2-trifluoroethyl methacrylate (TFEMA), and surprisingly methyl-2-(trifluoromethyl) acrylate], known not to homopolymerise under radical conditions [49]. They later modified the end-group of PVDF with azide to prepare various functional polymers [50]. These authors then studied the effects of metals and ligands by employing a series of metal carbonyls in the ITP of VDF and block copolymerisation of VDF [51]. Despite the advances of these studies, a major drawback of this procedure stems from the fact that it is of academic interest only and can not be scaled up for commercial applications. Nonetheless, these interesting results could lead to the synthesis of a wide range of poly(VDF)-*b*-poly(M) block copolymers (where ‘M’ could be VAc, vinyl chloride, acrylonitrile, methyl acrylate, S or butadiene).

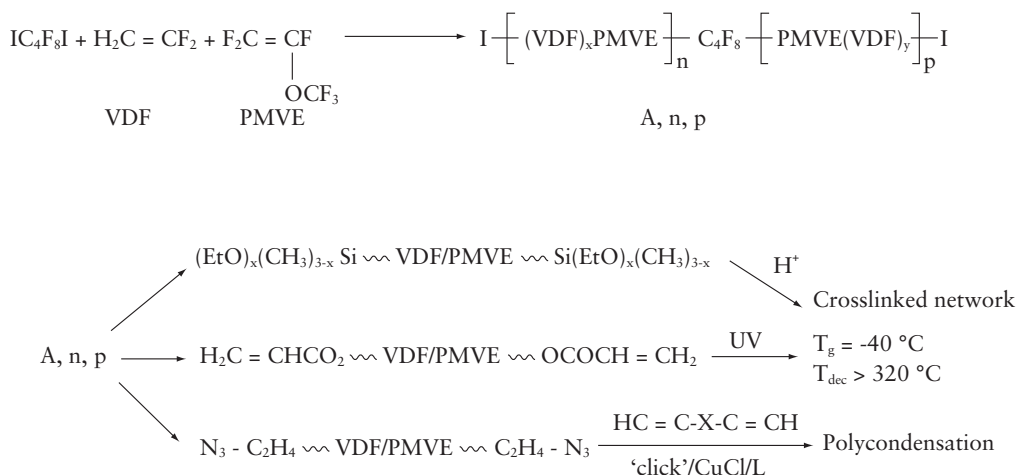
6.3.1.2 Iodine Transfer Copolymerisation of Vinylidene Fluoride and Perfluoroalkyl Vinyl Ethers

Non-homopolymerisable perfluoroalkyl vinyl ethers (PAVE) ($r_{\text{PAVE}} = 0$), can be easily copolymerised with either TFE or VDF to yield random copolymers which are semicrystalline or amorphous (with reduced crystallinity compared with PTFE and PVDF) [52]. The key innovative aspect of these polymers is producing materials with T_g lower than $-40\text{ }^\circ\text{C}$ for potential low-temperature applications [53], along with good thermal stability for potential future application in aeronautics and automotive industries.

Despite extensive reports of successful conventional radical copolymerisations of VDF (or TFE) and PAVE [52], only one patent and one publication mention the controlled radical copolymerisation of VDF with PMVE *via* ITP in conjunction with $\text{C}_6\text{F}_{13}\text{I}$ or α,ω -diiodoperfluoroalkanes as the CTA [54] (**Scheme 6.4**) in water, without using any surfactant. The linear molar mass-monomer conversion relationship confirmed the controlled nature of the polymerisation [54]. Using the signals assigned to the central $-\text{C}_4\text{F}_8$ group of the CTA as a marker, ^{19}F -nuclear magnetic resonance (NMR) spectroscopy allowed us to determine the MW and to unequivocally identify the end-groups (which are exclusively composed of VDF-I). Indeed, the higher the MW, the lower the $-\text{CH}_2\text{CF}_2-\text{I}$ content and the higher the $-\text{CF}_2\text{CH}_2-\text{I}$ content. The latter could not reactivate chains because the bond dissociation energy of $-\text{CH}_2-\text{I}$ is higher than that of $-\text{CF}_2-\text{I}$ [54]. The resulting poly(VDF-*co*-PMVE) copolymers exhibit low T_g values (approximately $-60\text{ }^\circ\text{C}$) and satisfactory thermal stability upon crosslinking by the chemical modification of these diiodides into original telechelic *bis*(hydroxyl) [55],

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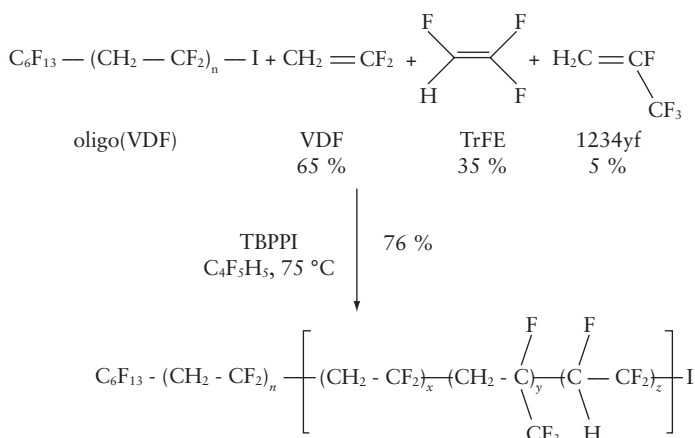
diazido [56], diacrylates [55], *bis*(triethoxysilanes) [57], *bis*(methyldiethoxysilanes) [57] and poly(VDF-*co*-PMVE) copolymers.



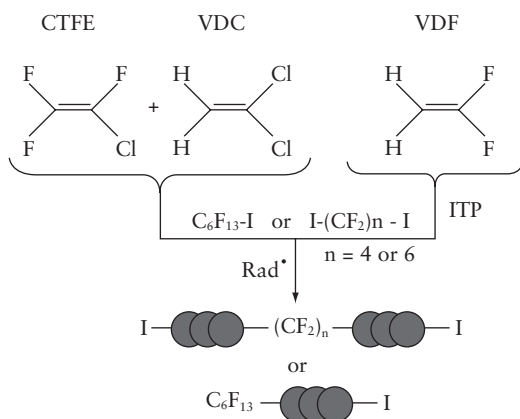
Scheme 6.4 Iodine transfer copolymerisation of VDF with PMVE in the presence of 1,4-diiodoperfluorobutane as the CTA, followed by chemical modification and crosslinking. Adapted from C. Boyer, B. Ameduri and M.H. Hung, *Macromolecules*, 2010, **43**, 8, 3652 [54]

Ameduri and Patil developed a method to synthesise block copolymers *via* the controlled free radical copolymerisation of trifluoroethylene (TrFE) with another fluoromonomer, such as VDF or 2,3,3,3-tetrafluoroprop-1-ene (1234), in the presence of 1-iodo-PVDFmacroCTA (**Scheme 6.5**) [58].

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Scheme 6.5 Synthesis of PVDF-*b*-poly(VDF-*ter*-TrFE-*ter*-1234) block copolymers by ITP, where 2,3,3,3-tetrafluoroprop-1-ene is 1234 and *tert*-butylhydroperoxide is TBPPI. Reproduced with permission from B. Ameduri and Y. Patil, inventors; Arkema and CNRS, assignee; US2014/015461, 2014 [58]



Scheme 6.6 Synthesis of fluorinated macroCTA by ITP of various halogenated monomers where VDC is vinylidene chloride. Reproduced with permission from G. Lopez, A. Thenappan and B. Ameduri, *ACS Macro Letters*, 2015, 4, 1, 16. ©2015, American Chemical Society [59]

Recently, Lopez and co-workers reported the synthesis of various fluorinated macroCTA based on VDF, CTFE, or CTFE and VDC to synthesise block polymers by ITP (Scheme 6.6) [59].

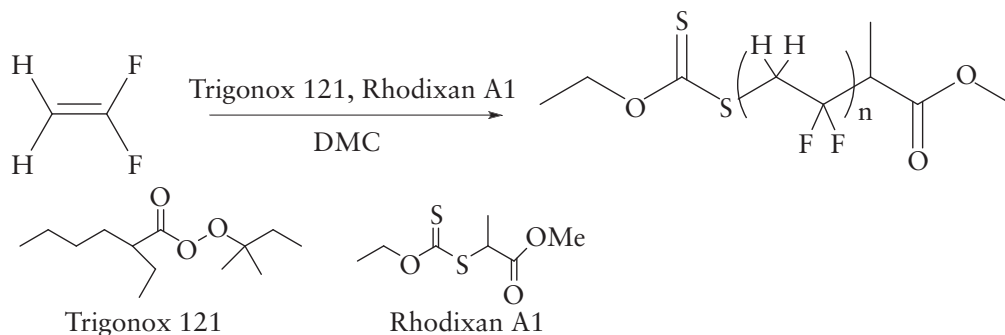
In summary, ITP was the first RDRP that led to commercial production in the fluoropolymer industry, pioneered by the Daikin Company and followed by Dupont and Solvay Specialty Polymers. Further academic studies and improvements have been carried out.

6.3.2 Reversible Addition-Fragmentation Chain Transfer/Macromolecular Design via the Interchange of Xanthates Polymerisation of Fluoroalkenes

RAFT/MADIX polymerisation, pioneered by the Rhodia Company [21, 23] for the RDRP of VAc, has recently emerged as one of the most promising RDRP techniques because of its tolerance towards diverse functional groups, applicability to a wide range of vinyl monomers and its less stringent experimental conditions [28]. The fundamentals of RAFT polymerisation were recently reviewed [28]; thus, the subsection below focuses on recent advances towards the synthesis of specifically designed fluorinated copolymers *via* MADIX.

6.3.2.1 Reversible Addition-Fragmentation Chain Transfer/Macromolecular Design via the Interchange of Xanthates Homopolymerisation of Fluoromonomers

The development of initiating systems to achieve the RDRP of fluoromonomers, especially VDF, is still very challenging. Guerre and co-workers developed an efficient protocol for the first MADIX polymerisation of VDF in DMC using O-ethyl-S-(1-methoxycarbonyl)ethylthiocarbonate as the CTA (Scheme 6.7) [60].

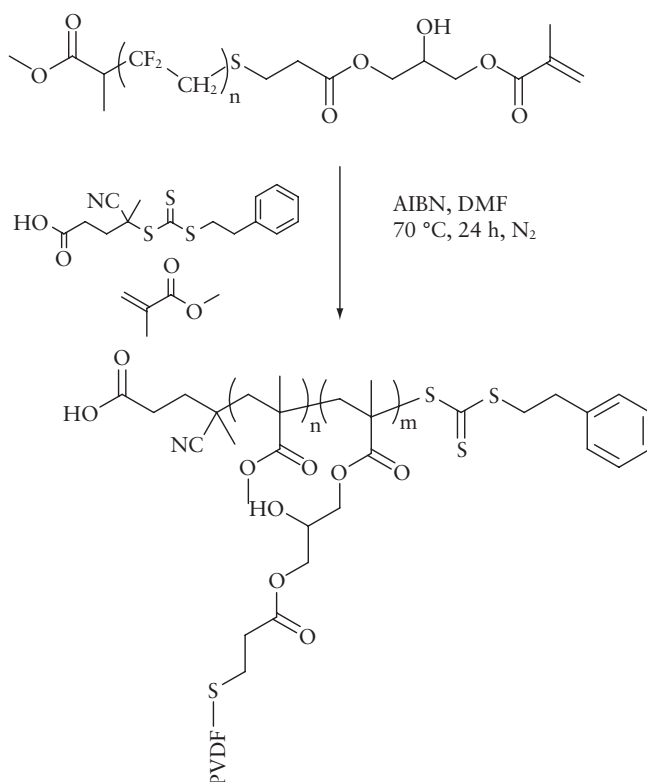


Scheme 6.7 Synthesis of PVDF by the RAFT/MADIX polymerisation of VDF. Reproduced with permission from M. Guerre, B. Campagne, O. Gimello, K. Parra, B. Ameduri and V. Ladmiral, *Macromolecules*, 2015, 48, 21, 7810. ©2015, American Chemical Society [60]

A comprehensive NMR study was performed to determine the end-group functionality of the polymer, mainly $-\text{CH}_2\text{CF}_2-\text{SC}(\text{S})\text{OEt}$ and $-\text{CF}_2\text{CH}_2-\text{SC}(\text{S})\text{OEt}$. This technique allowed us to prepare relatively well-defined PVDF. Detailed chain-end analysis using matrix-assisted laser desorption/ionisation (MALDI)-time-of-flight (TOF) mass spectrometry (MS) as well as ^1H , ^{19}F and HETCOR ^1H - ^{19}F -NMR established that VDF reverse additions and chain transfer reactions to the solvent (DMC) are responsible for a significant loss of CTA and the accumulation of unreactive polymer chains in the reaction medium, leading to a loss of control of the polymerisation [60].

Subsequently, the chemical modification of the xanthate end-group of the above-mentioned PVDF into thiols *via* two strategies was carried out (namely, aminolysis and elimination using sodium azide). The thiols were then immediately added onto the acrylate functionalities of 3-(acryloyloxy)-2-hydroxypropyl methacrylate *via* regioselective thia-Michael addition to form new PVDF-methacrylate macromonomers. Results revealed that the aminolysis procedure gave better coupling efficiency and better defined PVDF-methacrylate macromonomers. Thus, the synthesised PVDF-methacrylate macromonomer was then copolymerised with methyl methacrylate (MMA), resulting in the complete conversion of the macromonomer and synthesis of novel block copolymers (Scheme 6.8) [61]. In addition, such PVDF-xanthates are precursors for PVDF-*b*-polyvinyl acetate block copolymers (Scheme 6.9) [62].

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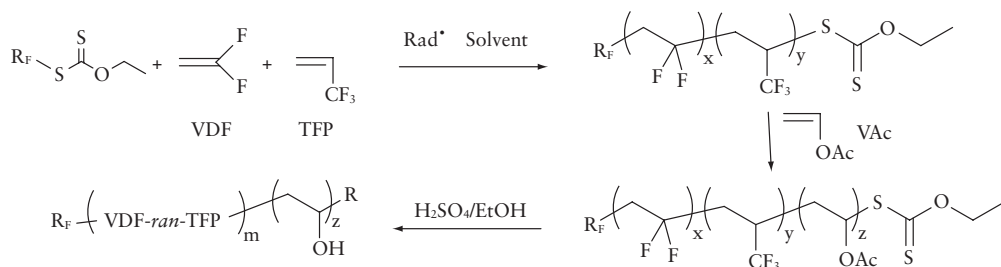


Scheme 6.8 RAFT copolymerisation of a PDVF-methacrylate macromonomer with MMA (AIBN: azobisisobutyronitrile). Adapted from M. Guerre, B. Ameduri and V. Ladmiral, *Polymer Chemistry*, 2016, 7, 2, 441 [61]

6.3.2.2 Reversible Addition-Fragmentation Chain Transfer/ Macromolecular Design via the Interchange of Xanthates Copolymerisation of Fluoromonomers

Kostov and co-workers developed a fluorinated xanthate, C₆F₁₃C₂H₄OCOCH(CH₃)SC(S)OEt, to achieve efficient MADIX copolymerisation of VDF with 3,3,3-trifluoropropene (TFP) [62]. The resulting fluorinated poly(VDF-*co*-TFP)-macroxanthate was subsequently chain extended by a further MADIX polymerisation of VAc to produce novel poly(VDF-*co*-TFP)-*b*-oligo(VAc) block copolymers (Scheme 6.9).

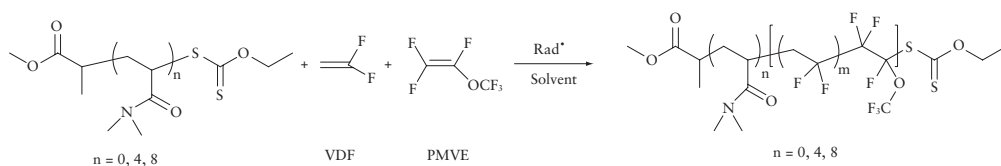
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Scheme 6.9 Sequenced MADIX terpolymerisation of VDF, TFP and VAc controlled by a fluorinated xanthate for the synthesis of poly(VDF-*co*-TFP)-*b*-oligo(VAc) block copolymers further hydrolysed into original surfactants. Adapted from G. Kostov, F. Boschet, J. Buller, L. Badache, B. Ameduri and S. Brandstadter, *Macromolecules*, 2011, **44**, 7, 1841 [62]

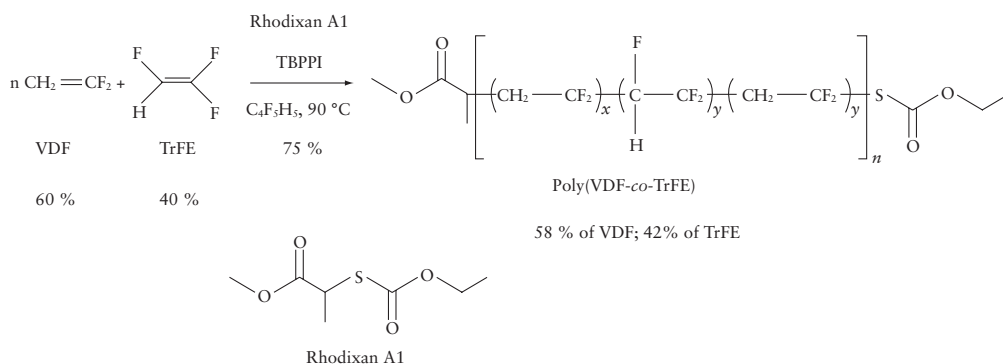
Hydrolysis of the oligo(VAc) segment under acidic conditions produced amphiphilic poly(VDF-*co*-TFP)-*b*-oligo(vinyl alcohol) diblock copolymers. These block oligomers act as novel surfactants [63] endowed with low critical micellar concentrations and surface tensions (17 mN.m⁻¹ for 0.5% of copolymer in water), similar to perfluorooctanoic acid (PFOA). These block copolymers could be alternatives to commercially available surfactants such as PFOA and perfluorooctane sulfonic acid (regarded as toxic, persistent and able to be bioaccumulated, and even suspected to be mutagenic) due to their small size and the high stability of the perfluorinated groups [63–65].

The xanthate-mediated MADIX polymerisation was subsequently successfully extended to develop polymeric surfactants for scCO₂ media. The developed surfactants displayed very interesting CO₂-philicity behaviour. The synthesis involves the copolymerisation of VDF and PMVE from hydrophilic poly(*N,N*-dimethylacrylamide) macroRAFT agents (Scheme 6.10) [66].



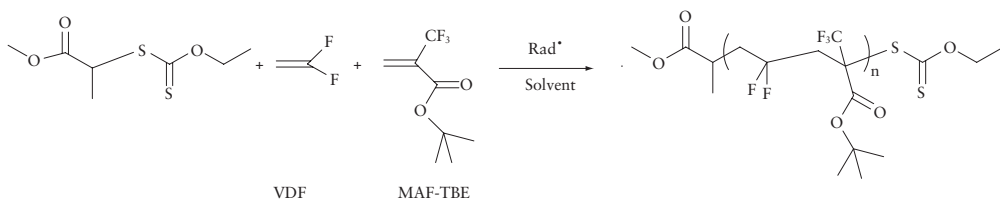
Scheme 6.10 Synthesis of poly(*N,N*-dimethylacrylamide) (PDMAc)-*b*-poly(VDF-*co*-PMVE) block copolymers by RAFT/MADIX copolymerisation of VDF and PMVE from a macroxanthate based on oligo(*N,N*-dimethyl acrylamide) oligo(DMAc) for the synthesis of block copolymers. Adapted from E. Girard, J.D. Marty, B. Ameduri and M. Destarac, *ACS Macro Letters*, 2012, **1**, 2, 270 [66]

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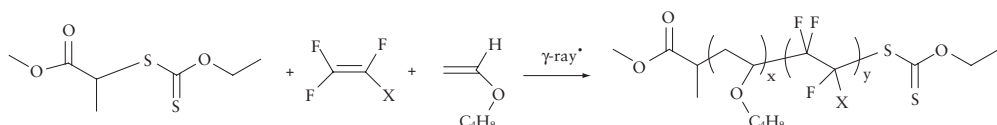
Scheme 6.11 Synthesis of block copolymers by MADIX polymerisation of VDF and TrFE. Reproduced with permission from B. Ameduri and Y. Patil, inventors; Arkema and CNRS, assignee; US2014/0154611, 2014 [58]

A similar strategy was successfully applied for the controlled radical copolymerisation of VDF and TrFE for the development of electroactive polymers (**Scheme 6.11**) [58]. Arkema claimed the successful synthesis of block copolymers containing VDF, TrFE and 1234yf units by MADIX polymerisation [58]. In addition, another comonomer, *tert*-butyl 2-trifluoromethacrylate (MAF-TBE) (which can not be homopolymerised under radical conditions) was copolymerised with VDF, using *bis*(4-*tert*-butylcyclohexyl) peroxydicarbonate as the initiator and *O*-ethyl-*S*-(1-methyloxycarbonyl) ethyl xanthate as the CTA *via* RAFT/MADIX polymerisation (**Scheme 6.12**), producing copolymers with controlled molar masses ranging between 1,500 to 40,000 g.mol⁻¹ and *Đ* lower than 1.8 [67]. Chain extension of these poly(VDF-*co*-MAF-TBE) copolymers bearing a xanthate end-group was carried out either with VAc or VDF to produce poly(VDF-*co*-MAF-TBE)-*b*-poly(VAc) and poly(VDF-*co*-MAF-TBE)-*b*-PVDF block copolymers, respectively.



Scheme 6.12 Radical copolymerisation of VDF with MAF-TBE controlled by *O*-ethyl-*S*-(1-methyloxycarbonyl) ethyl xanthate. Adapted from Y. Patil and B. Ameduri, *Polymer Chemistry*, 2013, 4, 9, 2783 [67]

Interestingly, such PVDF-based fluorinated copolymers have successfully been employed as compatibilisers for the preparation of poly(VDF-*co*-HFP) copolymer/functional silica nanocomposites, for use as novel proton exchange membrane fuel cells, by reactive extrusion [68]. The synthesis of these composites involved the *in situ* generation of the inorganic phase (*via* sol-gel chemistry from mercaptopropylethoxysilane). For the best performance, the compatibiliser has to be incorporated between the organic and inorganic phases. The resulting composites bearing mercaptan functionalities were oxidised into SO₃H groups under various conditions. The resulting original membranes exhibited a theoretical ion exchange capacity of approximately 2 meq.g⁻¹ (whereas the experimental ones ranged between 1.0 and 1.3 meq.g⁻¹) and proton conductivities of these membranes reached 30–80 mS.cm⁻¹ at room temperature (RT) and 100% RH. Interestingly, their water swelling rates were unexpectedly lower than that of commercially available Nafion[®] 212 [68]. Liu and co-workers [69, 70] (Liu, 2011 #1236) reported the MADIX copolymerisations of CTFE (or HFP) with *n*-butyl vinyl ether (BVE) initiated under ⁶⁰Co γ-ray irradiation in the presence of *S*-benzyl *O*-ethyl dithiocarbonate (**Scheme 13**). The synthesised poly(CTFE-*alt*-BVE) copolymers were used as macroCTA for the chain extension of VAc, leading to poly(CTFE-*alt*-BVE)-*b*-poly(VAc) diblock copolymers [69], whereas the poly(HFP-*alt*-BVE) copolymer end-capped with a sulfonic acid group was prepared by oxidation of the xanthate end-group of the poly(HFP-*alt*-BVE) copolymer [70].



Scheme 6.13 Xanthate-mediated copolymerisation of HFP (and/or CTFE) and BVE under ⁶⁰Co γ-ray irradiation. Adapted from L. Liu, D. Lu, H. Wang, Q. Dong, P. Wang and R. Bai, *Chemical Communications*, 2011, **47**, 27, 7839 and P. Wang, J. Dai, L. Liu, Q. Dong, B. Jin and R. Bai, *Polymer Chemistry*, 2013, **4**, 6, 1760 [69, 70]

6.3.2.3 Reversible Addition-Fragmentation Chain Transfer (Co)Polymerisation of Fluoromonomers Controlled by Trithiocarbonates

Wang's team [71] synthesised a telechelic poly(VDF-*co*-HFP) copolymer by RDRP and then used it as a macroCTA for the subsequent RAFT polymerisation of a methacrylate imidazolium to prepare a series of triblock copolymers composed of poly(VDF-*co*-

HFP) and an ionic liquid segment composed of an imidazolium methacrylate monomer. The authors observed that due to the enhanced segmental mobility, the polymers bearing trifluorosulfonate counterions displayed higher ionic conductivities than their BF_4^- homologues. The temperature dependence of the ion mobilities of the triblock copolymers, as described using a Vogel–Tamman–Fulcher equation, indicates a strong correlation between ion conduction and polymer segmental dynamics.

6.3.3 Atom Transfer Radical Polymerisation of Fluoroalkenes

Wang and co-workers [72] reported the unexpected controlled radical copolymerisation of CTFE with chloromethylstyrene (CMS) using ATRP between an electron-rich CMS inimer (that acts as both a monomer and an initiator) and an electron-withdrawing monomer (CTFE) that yielded hyperbranched poly(CTFE-*co*-CMS) copolymers. The authors claimed that ATRP occurred on the chlorine atoms of CMS but surprisingly did not occur from CTFE. The attempts to homopolymerise CTFE by ATRP systematically failed, favouring the idea that the poly(CTFE-*co*-CMS) copolymers exhibit an alternating structure, evidenced by elemental analyses. This hyperbranched polymer, soluble in common organic solvents, was amorphous with a T_g of 88 °C [intermediate between those of poly(CTFE) and polystyrene (PS), 57 and 100 °C, respectively].

In conclusion, among the RDRP methods employed for the synthesis of fluoropolymers from fluoroalkenes, ITP, RAFT/MADIX polymerisation has emerged as the best possible technique. Controlled polymerisation of fluoroalkenes has the potential to lead to many exciting new materials with unique properties.

6.4 Controlled Radical Polymerisation of Fluorinated Acrylates/Methacrylates/Styrenes

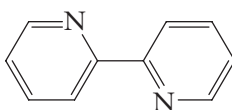
6.4.1 Nitroxide-mediated Polymerisation of Fluorinated Acrylates/Methacrylates

NMP is based on the termination of propagating radicals to 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-based organic compounds. In this case, the polymer chains contain TEMPO-end-groups. There are only a few examples of the TEMPO-mediated polymerisation of fluorinated acrylates (FA)/furfuryl methacrylates (FMA). In 2012, Barth and co-workers [73] reported the TEMPO-mediated polymerisation of 1H,1H,2H,2H-tridecafluorooctyl methacrylate in bulk.

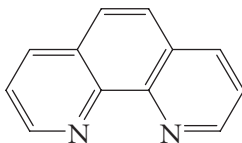
Recently, Martinelli and co-workers [74] prepared a series of amphiphilic triblock copolymers based on PS modified with polyethylene glycol (PEG), polysiloxane and perfluoroalkyl side chains. In this case, the triblock copolymers had been prepared by a sequential NMP process. However, the surface composition did not follow the sequential position of different blocks as observed from elemental analysis. The migration of perfluoroalkyl side chains towards the surface predominated, which decreased the surface energy of the block copolymer.

6.4.2 Atom Transfer Radical Polymerisation of Fluorinated Acrylates/ Methacrylates

The ATRP process is based on the reversible electron transfer between a propagating radical and a transition metal complex. In this case, an alkyl halide is used as the initiator and a transition metal complex acts as the catalyst. **Scheme 6.14** displays the chemical structures of some ligands used to prepare the transition metal complex for the successful polymerisation of FA/FMA. There are reports on the development of fluorinated homopolymers, random copolymers and block copolymers using the ATRP process, which also offers the scope to prepare polymer brushes grown on a substrate. Researchers took this opportunity to modify various surfaces and termed the polymerisation process surface-initiated atom transfer radical polymerisation (siATRP). There is another category of the ATRP process named activators generated by electron transfer (ARGET)-ATRP, where the catalyst is generated in the reaction medium.

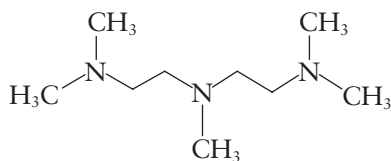


2,2'-Bipyridine (I)

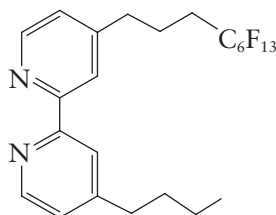


1,10-Phenanthroline (II)

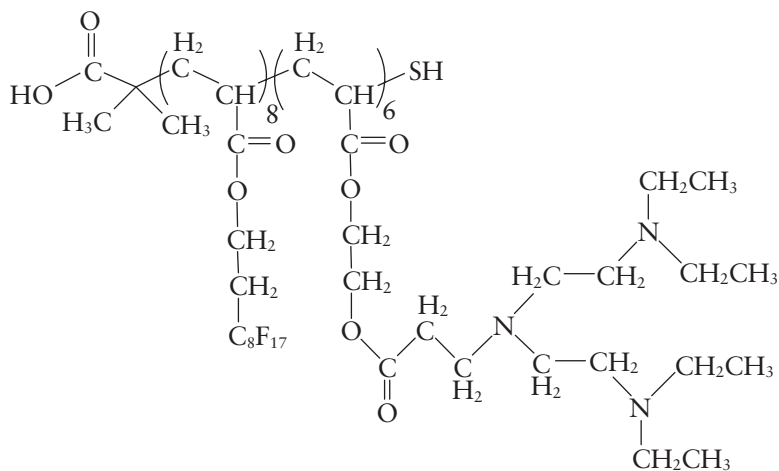
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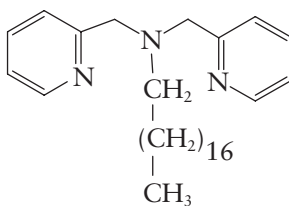
N,N,N',N'',N'''-Pentamethyldiethylene triamine (III)



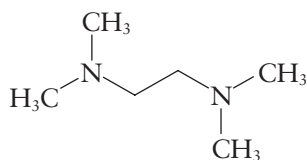
4,4'-Di(tridecafluoro-1,1,2,2,3,3-hexahydrononyl)-2,2'-bipyridine (IV)



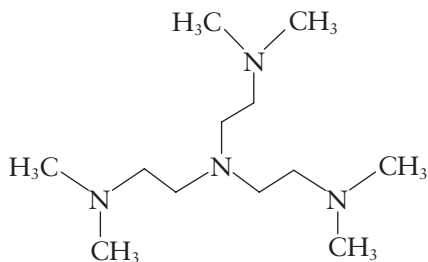
TEDETA (V)



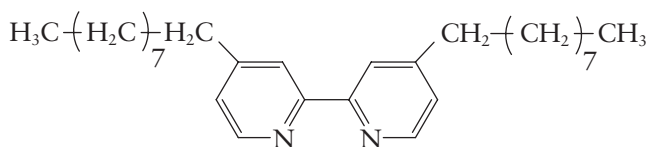
Bis(2-pyridyl methyl) octadecylamine (VI)



N,N,N',N'-Tetramethylethylenediamine (VII)



Tris[2-(dimethylamino)ethyl] amine (VIII)



4,4'-Dinonyl-2,2'-dipyridyl (IX)

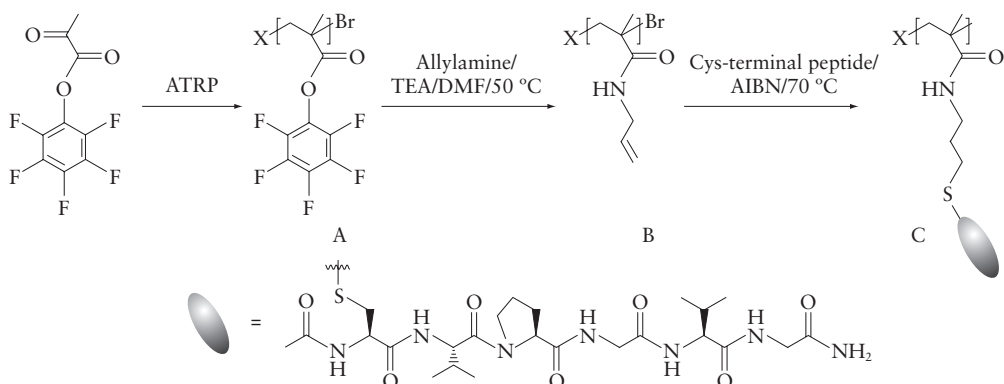
Scheme 6.14 Chemical structures of the ligands used in the ATRP of FA/FMA. The roman numerals denote different ligands which are mentioned in the text

6.4.2.1 Fluorinated Homo and Random Copolymers via Atom Transfer Radical Polymerisation

In 2011, He and co-workers [75] reported the ATRP of TFEMA. In this case, the authors studied the polymerisation using different types of ligands such as 'I', 'III' and 'VIII'. Interestingly, the polymer displayed more controlled MW and narrow $\bar{D}$ with 'I' as the ligand, compared with 'III'. However, the polymerisation using 'VIII' as the ligand led to lower monomer conversion with gel formation. The inequality between the activation and deactivation process with ligands of different

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denticity (the number of donor groups in a single ligand that bind to a central atom in a coordination complex) was supposedly responsible for this phenomenon. The ATRP of pentafluorophenyl methacrylate (PFPMA) was reported by Singha and co-workers [76]. The polymerisation was carried out using ligand 'III' (Scheme 6.15). Interestingly, the polymer had an activated ester which could be easily replaced by a primary amine. Using AIBN as a thermal radical source, the peptide could be grafted onto the polymer with a 50% grafting density, as demonstrated by scanning electron microscopy (SEM) and NMR analysis.

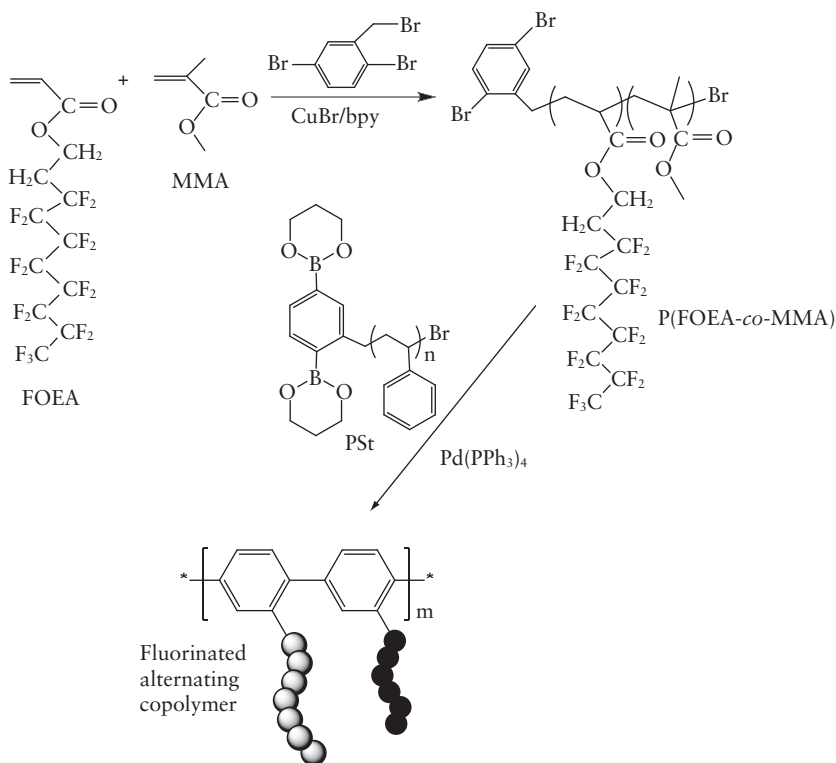


Scheme 6.15 Preparation of biofunctionalised polymethacrylate *via* tandem 'ester–amide/thiol–ene' postpolymerisation modification of poly(PFPMA) obtained by ATRP (DMF: *N,N*-dimethylformamide and TEA: triethylamine).

(A) poly(PFPMA), (B) poly(allyl methacrylamide) and (C) peptide-grafted poly(allylmethacrylamide). Reproduced with permission from N.K. Singha, M.I. Gibson, B.P. Koiry, M. Danial and H-A. Klok, *Biomacromolecules*, 2011, **12**, 8, 2908. ©2011, American Chemical Society [76]

Durmaz and co-workers reported the preparation of a fluorinated alternating copolymer using ATRP and Suzuki coupling processes [77]. In this case, a fluorinated copolymer composed of perfluorooctylethyl acrylate (FOEA), MMA and PS was prepared separately *via* the ATRP process. These were used as macromonomers in Suzuki polycondensation reactions, producing the alternating copolymer as shown in Scheme 6.16.

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Scheme 6.16 Preparation of a fluorinated alternating copolymer *via* consecutive ATRP and Suzuki coupling reactions. Adapted from Y.Y. Durmaz, E.L. Sahkulubey, Y. Yagci, E. Martinelli and G. Galli, *Journal of Polymer Science, Part A: Polymer Chemistry*, 2012, 50, 23, 4911 [77]

6.4.2.2 Fluorinated Block Copolymers via Atom Transfer Radical Polymerisation

Due to certain unique properties, fluorinated block copolymers have attracted considerable research interest in recent years. In most cases, researchers took advantage of the amphiphilic nature of diblock fluoropolymers (DBF) which let them produce a wide range of morphologies in water or organic solvents. The amphiphilicity in DBF arises due to the presence of a hydrophobic fluorinated block and any hydrophilic segment. In 2009, a general approach was reported by Lee and co-workers [78]; they prepared an amphiphilic DBF composed of a hydrophobic poly(1H,1H-dihydroperfluorooctyl methacrylate) and polyethylene oxide (PEO), a well-known hydrophilic polymer. In this case, the well-defined DBF had been prepared *via* ATRP

using PEO–Br as the macroinitiator. The DBF displayed different morphologies upon self-assembly in different organic solvents. The DBF adopted micellar morphology with hydrodynamic radii in the range of 60–300 nm in a chloroform solvent; however, vesicles were formed in DMF and lamellar morphology was obtained in methanol. The preparation of PEO-based amphiphilic DBF was also reported by Jiang and co-workers [79], who adopted ATRP to polymerise 2,2,3,4,4,4-hexafluorobutyl methacrylate (HFBMA) and used the resulting fluorinated polymer as a macroinitiator to polymerise hydrophilic oligo(ethylene glycol) methyl ether methacrylate. In this case, the authors considered the thermoresponsive property of the PEG segment and demonstrated the responsive nature of the micelles (30–40 nm at RT and 40–300 nm at 60 °C) formed by the DBF in its aqueous solution. Interestingly, a cotton fabric dipped in the micellar solution at RT showed a water contact angle (WCA) of 150° after drying. However, when a dried cotton fabric was dipped in the hot micellar solution of DBF, it was quite hydrophilic. The same team [80] also used ATRP to prepare amphiphilic DBF composed of poly(2,2,3,4,4,4-hexafluorobutyl methacrylate) (PHFBMA) and polyglycidyl methacrylate (PGMA). This DBF, PHFBMA-*b*-PGMA was made amphiphilic by the ring-opening reaction of epoxy groups in PGMA. In this case, the DBF self-assembled as hollow microspheres in water with a mean diameter of 50–80 nm. Peng and co-workers [81] prepared DBF with a series of FA/FMA and *tert*-butyl acrylate (*t*BA). The hydrolysis reaction converted the *tert*-butyl groups to –COOH making the DBF amphiphilic in nature. The spontaneous self-assembly of DBF in water produced micellar morphology in the size range of 20–45 nm in diameter. Interestingly, the micelles with a fluorinated core provided a strong signal upon magnetic resonance imaging (MRI) analysis. Thus, the DBF was successfully used as a ¹⁹F-MRI imaging agent. In addition to the above examples of amphiphilic DBF, a non-amphiphilic DBF based on PS and PHFBMA was prepared by adopting ATRP [82]. In this case, the authors studied the self-aggregation phenomena of the prepared PS-*b*-PHFBMA in a tetrahydrofuran (THF)/EtOAc mixture. As EtOAc is a non-solvent for the fluorinated block, the DBF showed a transition in morphology from micelles (90–100 nm) to vesicles (150–200 nm) upon the gradual increase of EtOAc content.

Apart from the DBF, ATRP has also been successfully used to prepare a triblock fluoropolymer (TBF). In this regard, the approach by Guo and co-workers deals with a simple synthetic route to prepare amphiphilic ABC-type TBF [83]. In this case, the authors prepared a PEO-based macroinitiator to polymerise S and 2-(perfluorohexyl) ethyl methacrylate (FHEMA) *via* consecutive ATRP. Importantly, all the prepared TBF had controlled MW and moderately narrow *Đ* (1.31–1.47). The TBF showed very good protein resistance due to the presence of the PEO-segment.

Rabnawaz and Liu [84] reported a novel TBF which is simultaneously photocleavable and photocrosslinkable. The amphiphilic triblock terpolymer PEO-*ortho*-nitrobenzyl

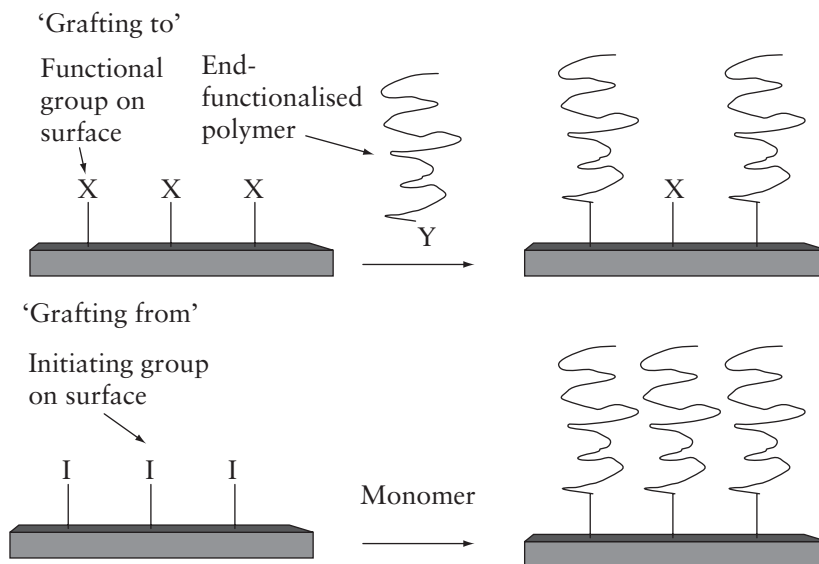
(ONB)-poly[2-(perfluorooctyl) ethyl methacrylate] (PFOEMA)-*block*-poly(2-cinnamoyloxy ethyl methacrylate) (PCEMA) was prepared *via* consecutive ATRP using PEO-ONB-Br as the macroinitiator. In this case, the ONB unit is photocleavable and PCEMA is photocrosslinkable. The fluorinated segment, PFOEMA, was incorporated to achieve superhydrophobicity and oleophobicity. Upon photocrosslinking, the H₂O and CH₂I₂ contact angles increased to 154° and 136° from 52° and 32°, respectively, in the micellar films.

Polymers bearing polyhedral oligomeric silsesquioxanes (POSS) moieties are important, mainly because of their excellent surface properties. Thus, an improvement in surface properties is expected in a POSS-containing fluorinated polymer. Qiang and co-workers [85] adopted ATRP to prepare POSS-containing star-shaped polymethyl methacrylate (PMMA)-*b*-poly(2,2,2-trifluoroethyl methacrylate) (PTFEMA). In this case, POSS-Cl was used as an ATRP initiator to prepare the star-shaped DBF, which displayed a honeycomb morphology resulting in superior hydrophobicity (WCA 95–110°).

6.4.2.3 Hybrid Fluoropolymers and Brushes via Atom Transfer Radical Polymerisation

siATRP is one of the important aspects of ATRP [26a]. It offers the scope to prepare well-defined hybrid polymers and polymer brushes with improved properties. There are two types of approaches for siATRP, known as ‘grafting to’ and ‘grafting from’. The former approach deals with the attachment of a preformed polymer to a substrate. In this case, the polymer should have a functional end-group to bind a substrate. The latter approach enables control of the growth of the polymer chain from an initiator-functionalised surface (Scheme 6.17) [86]. Both approaches have attracted considerable attention in order to develop new macromolecular architectures.

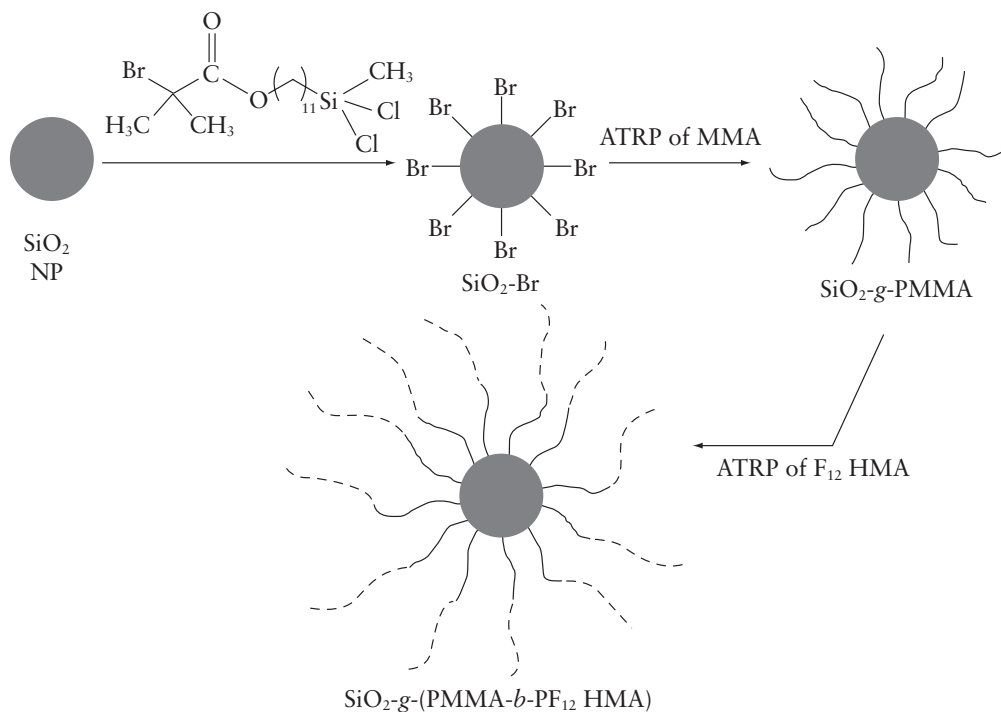
Huang and He [87] adopted the ‘grafting from’ approach to develop a hybrid DBF *via* siATRP from a nano-SiO₂ surface. In this case, nano-SiO₂ was chemically modified to be used as an ATRP initiator. The consecutive polymerisation of MMA and dodecafluoroheptyl methacrylate (F₁₂HMA) was carried out to prepare the hybrid fluoropolymer SiO₂-*g*-PMMA-*b*-PF₁₂HMA (Scheme 6.18).



Scheme 6.17 The preparation of polymer brushes *via* 'grafting to' and 'grafting from' approaches. Reproduced with permission from P.M. Mendes, *Chemical Society Reviews*, 2008, 37, 11, 2512. ©2008, Royal Society of Chemistry [86]

The hybrid DBF exhibited higher surface roughness and lower surface energy (10.97 mN/m) due to the accumulation of the fluorinated segment over the surface. In a similar fashion, Huang and co-workers [88] recently developed an amphiphilic hybrid fluoropolymer as SiO₂-g-polyethylene glycol methacrylate (PEGMA)-*b*-F₁₂HMA. The DBF produced spherical nanoparticles (NP) (~150 nm in water and ~170 nm in a THF solution) due to self-assembly. Functionalised nano-SiO₂ was also used as an ATRP initiator by Yu and co-worker [89]. In this case, the hybrid DBF was prepared by the consecutive ATRP of 3-methacryloxypropyltrimethoxysilane and HFBMA using SiO₂-Br as the initiator. The hybrid DBF created a nanophase roughness as observed from SEM and AFM analyses. As a result, it displayed superhydrophobicity with WCA in the range of 135 to 161°.

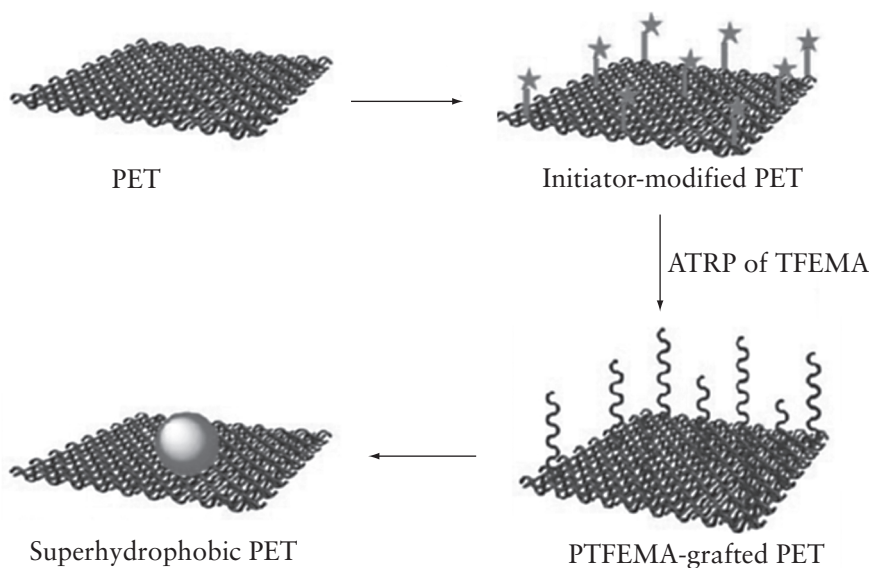
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Scheme 6.18 Preparation of a SiO₂-grafted fluorinated block copolymer *via* the siATRP process. Reproduced with permission from H. Huang and L. He, *RSC Advances*, 2014, 4, 25, 13108. ©2014, Royal Society of Chemistry [87]

Apart from the hybrid polymers, the preparation of fluoropolymer brushes is of great significance as they exhibit interesting properties. Recently, PTFEMA brushes on polyethylene terephthalate (PET) fabrics were synthesised *via* siATRP using a ‘grafting from’ approach [90]. Interestingly, the resulting PET fabrics displayed anti-fouling and superhydrophobic properties (Scheme 6.19).

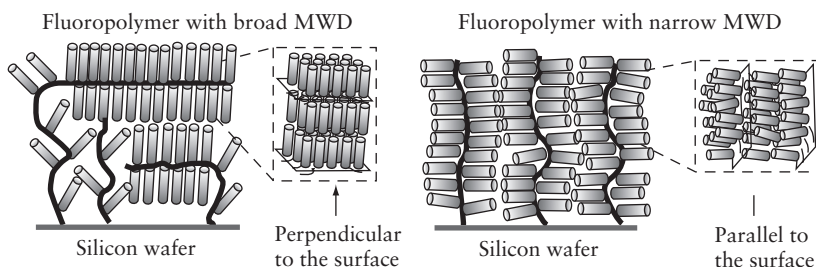
Shinohara and co-workers [91] reported the preparation of fluoropolymer brushes on nanoimprinted surfaces. Nanoimprinting (NI) is a technology used to fabricate nanotopography on a polymer surface. In this case, a regular pillar pattern was created on a poly[MMA-*co*-2-(2-bromoisobutyryloxy) ethyl methacrylate] thin film *via* an NI process. The siATRP of FOEA from that imprinted thin film produced a nanostructured surface covered with the fluoropolymer. The polymeric film displayed superhydrophobicity due to the synergistic effect of surface geometry from NI and low surface energy provided by the fluorinated segments.



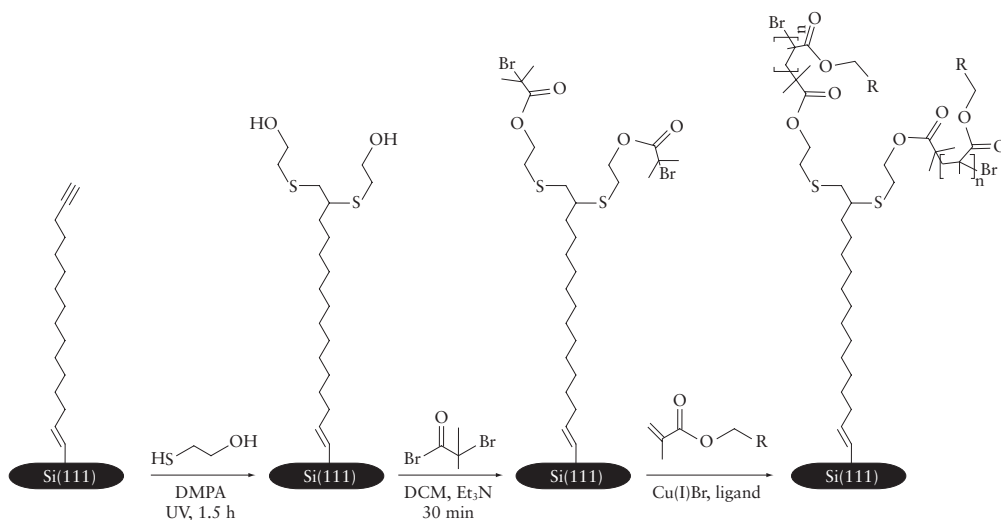
Scheme 6.19 Development of superhydrophobic surface *via* siATRP of TFEMA on PET fabrics. Reproduced with permission from C-H. Xue, X-J. Guo, J-Z. Ma and S-T. Jia, *ACS Applied Materials and Interfaces*, 2015, 7, 15, 8251. ©2015, American Chemical Society [90]

Silicon wafers have also been used as initiating surfaces for the polymerisation of fluoromonomers. The aggregation behaviour of polymer chains grown on flat surfaces like silicon wafers has attracted considerable research interest. The surface properties such as adhesion, friction and wettability can be tuned by the orientation of the fluoropolymer chains. According to Yamaguchi and co-workers [92], the molecular aggregation in a polymer brush was dependent on the dispersity. In the case of a polymer with a broad molecular weight distribution (MWD), the pendant fluorinated groups (R_f) were perpendicular to the surface (**Scheme 6.20**). On the other hand, the R_f groups were parallel to the surface when the polymer exhibited narrow $\bar{D}$. This parallel orientation of R_f groups resulted in lower water resistance compared with the polymer brush with perpendicular R_f groups.

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Scheme 6.20 Molecular orientation of fluorinated segments in a fluoropolymer brush prepared *via* siATRP on a silicon wafer. Reproduced with permission from H. Yamaguchi, M. Kikuchi, M. Kobayashi, H. Ogawa, H. Masunaga, O. Sakata and A. Takahara, *Macromolecules*, 2012, **45**, 3, 1509. ©2012, American Chemical Society [92]



Scheme 6.21 Surface functionalisation of a silicon wafer with polyfluoromethacrylates *via* a thiol–yne click reaction and ATRP (DCM: dichloromethane and DMPA: 2,2-dimethoxy-2-phenylacetophenone). Reproduced with permission from N.S. Bhairamadgi, S.P. Pujari, C.J.M. Rijn and H. Zuilhof, *Langmuir*, 2014, **30**, 42, 12532. ©2014, American Chemical Society [93]

The study by Bhairamadgi and co-workers [93] revealed that surface properties like friction and adhesion may be regulated by the number of fluorine atoms in the monomer. In this case, fluoropolymer brushes were prepared on a silicon wafer by the combination of a thiol–yne click reaction and ATRP (Scheme 6.21). The copolymerisation of ethyl methacrylate, TFEMA, HFBMA and 2-perfluorooctylethyl methacrylate produced polymer brushes with increasing numbers of F atoms per monomer (0, 3, 7 and 17). As expected, the fluoropolymer brushes displayed the lowest adhesion forces when the monomer contained the highest number of F atoms.

6.4.3 Activators Generated by Electron Transfer–Atom Transfer Radical Polymerisation of Fluoromonomers

According to the previous discussions, it is obvious that ATRP has achieved considerable success in the polymerisation of fluoromonomers; however, the process suffers some limitations in the case of industrial scale-up. The air sensitivity of the catalyst used in ATRP was found to be a big issue in prospective commercial processes. To overcome this issue, Matyjaszewski and co-workers [94] developed the ARGET-ATRP process where the catalyst Cu(I) complex is generated *in situ* by the reduction of a stable Cu(II) complex by reducing agents such as Cu(0), tin(II)2-ethylhexanoate [Sn(EH)₂], ascorbic acid and so on. Soon after this development, the process was established as a simple and versatile method in RDRP, and researchers took advantage for the simple preparation of tailor-made fluoropolymers.

An early approach was made by Sun and Liu [95] who prepared poly(HFBMA)-*b*-polyisobutyl methacrylate (PIBMA) *via* sequential ARGET-ATRP using Cu(0) as the reducing agent. The polymerisation was well controlled for the preparation of the macroinitiator, poly(HFBMA)-Br, and the DBF, poly(HFBMA)-*b*-PIBMA. In this case, DBF displayed lower surface energy and higher fluorine content at the polymer–air interface compared with the random copolymer. Due to the presence of the hydrophobic fluorinated segment, DBF self-assembled into micelles (100–150 nm) in water, showing core-shell morphology upon transmission electron microscopy analysis.

Recently, Zhan and co-workers [96] developed a novel approach to prepare tailor-made fluorinated hybrid materials by combining siATRP and ARGET-ATRP. In this case, a fluorinated copolymer, poly[butyl acrylate-*co*-2-(*N*-ethyl perfluorooctane sulfamido) acrylate] was synthesised *via* siARGET-ATRP using SiO₂–NH–Br as the initiator and Sn(EH)₂ as the reducing agent. Interestingly, the hybrid fluoropolymer displayed superhydrophobicity with a WCA of 170.3° and an anti-icing property due to the formation of a nanostructured morphology by the covalently bonded SiO₂ NP.

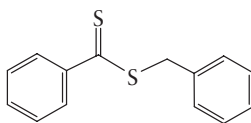
ARGET-ATRP has also been successfully applied for the emulsion polymerisation of fluoromonomers. Shu and co-workers [97] reported the emulsion polymerisation of TFEMA *via* ARGET-ATRP using disodium 4-[10-(2-bromo-2-methyl-propanoyloxy) decyloxy]-4-oxo-2-sulfonatobutanoate as both the initiator and surfactant (inisurf). In this case, ascorbic acid was used as the reducing agent.

In order to reduce the amount of transition metal catalyst required during ATRP, Jakubowski and co-workers [98] developed another process with continuous regeneration of the catalyst in the reaction medium. This process, termed activators regenerated by electron transfer (ARGET)-ATRP, requires very small amounts of Cu catalyst and a higher amount of reducing agent compared with the ARGET-ATRP process. ARGET-ATRP was also found to be successful in preparing fluorinated homopolymers and block copolymers. Schreiber and co-workers [99] employed ARGET-ATRP to prepare DBF containing 1H,1H,2H,2H-perfluorodecyl acrylate (FDA) and *n*-butyl acrylate or *t*BA. In this study, a fluorinated ligand F-N,N,N',N'-tetraethyldiethylenetriamine (TEDETA) ('V' in **Scheme 6.14**), derived from TEDETA, was successfully used to achieve a faster rate of polymerisation and narrow *D*. According to Zheng and co-workers [100], ARGET-ATRP was found to be successful for the emulsion (co)polymerisation of 2,2,3,4,4,4-hexafluorobutyl acrylate (HxFBA). In this study, a fluorinated acrylic copolymer consisting of MMA, HxFBA and 2-hydroxypropyl acrylate was prepared with narrow *D* using *O*-phenanthroline as the ligand.

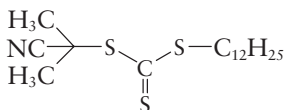
6.4.4 Reversible Addition-Fragmentation Chain Transfer Polymerisation of Fluoromonomers

The RAFT polymerisation process is a powerful tool for the preparation of polymers with controlled MW and well-defined architecture [28]. As mentioned above, this process requires a reversible CTA, such as dithio or trithio carbonates/carbamates, which takes part in the addition-fragmentation reaction with active and dormant chains. At the end of the polymerisation, the macromolecules contain RAFT functionality which can take part in a further chain extension reaction to enable block copolymer synthesis. Some terminated polymer chains or dead chains derived from the initiator are also formed. Thus, these systems require a higher ratio of RAFT agent to initiator in order to obtain a polymer with narrow *D*. This aspect was found to be challenging when preparing a fluoropolymer with well-defined architecture *via* the RAFT polymerisation technique. In this case, the selection of an appropriate RAFT agent is crucial. In addition to the xanthates reported in **Section 6.3.2.1**, **Scheme 6.22** displays some important RAFT agents used for the polymerisation of FA/FMA.

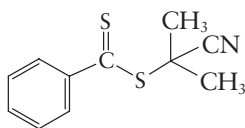
Recent Advances in the Reversible Deactivation Radical (Co)Polymerisation of Fluorinated Alkenes/Acrylates/Methacrylates/Styrenes



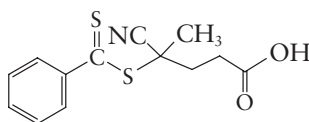
Benzyl dithiobenzoate (I)



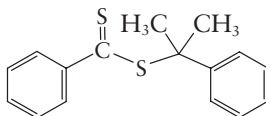
2-Cyano-2-propyl dodecyl trithiocarbonate (II)



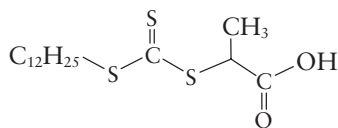
2-Cyano-2-propyl benzodithioate (III)



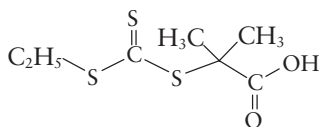
4-Cyanopentanoic acid dithiobenzoate (IV)



2-Phenyl-2-propyl dithiobenzoate (V)

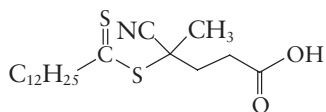


2-Dodecylthiocarbonothioylthio propionic acid (VI)

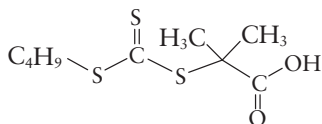


S-1-ethyl-S-(dimethyl acetic acid) trithiocarbonate (VII)

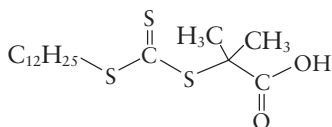
*Functional Polymers by Reversible Deactivation Radical Polymerisation:
Synthesis and Applications*



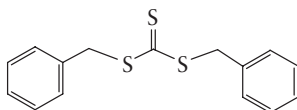
4-Cyano-4-(dodecyl sulfanylthiocarbonyl) sulfanyl pentanoic acid (VIII)



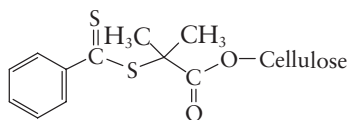
2-(Butylsulfanyl thiocarbonylsulfanyl)-2-methylpropionic acid (IX)



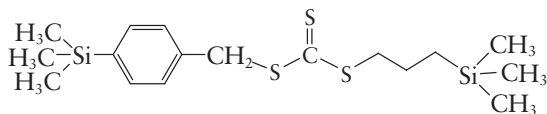
2-(Dodecylthiocarbonyl thioylthio)-2-methyl propionic acid (X)



Dibenzyl trithiocarbonate (XI)



Cellulose-CTA (XII)



4-(Trimethylsilyl)benzyl-4'-(trimethylsilyl)butane dithioate (XIII)

Scheme 6.22 Chemical structures of the RAFT agents used to polymerise fluorinated (meth)acrylates. The numbers refer to RAFT agents which are mentioned in the text

The polymerisation of 1H,1H,5H-octafluoropentyl acrylate (OFPA) was carried out in bulk using '1' as the RAFT agent [101]. Although the polymer had narrow $\bar{D}$, the conversion was only 53% at the polymerisation temperature of 70 °C. A similar observation was reported for the solution polymerisation of 2,2,3,3,4,4,4-heptafluorobutyl acrylate (HFBA) in 1,4-dioxane using RAFT agent '4' [102]. However, an increase in polymerisation temperature from 70 to 90 °C resulted in 90% conversion with a faster rate of polymerisation. In this case, the polymer had a broad $\bar{D}$. Gibson and co-workers [103] adopted the RAFT process to polymerise poly(FPMA) and subsequently employed postpolymerisation modification with primary amines. This approach paved the way for the synthesis of libraries of water-soluble functional polymers.

Some authors have employed protonated monomers to prepare fluorinated random copolymers *via* RAFT polymerisation techniques. Thus, they determined the reactivity ratios between the fluorinated and hydrocarbon monomers. In 2009, Zhang and co-workers [104] reported the RAFT copolymerisation of FHEMA and butyl methacrylate (BMA) in miniemulsion using 3 as the RAFT agent. According to their study, FHEMA had higher reactivity than BMA. In FHEMA, the propagating radical was more stabilised due to the electron-withdrawing inductive effect of the fluoroalkyl pendant group. However, a contradiction to this observation was reported for the RAFT-mediated copolymerisation of butyl acrylate (BA) with a fluorinated monomer, HFBA, using 11 as the RAFT agent [105]. The RAFT-mediated copolymerisation of BA with 2,2,2-trifluoroethyl acrylate (TFEA) and 2,2,3,3,3-pentafluoropropyl acrylate (PFPA) displayed a higher reactivity of the fluorinated monomers. However, HFBA displayed a lower reactivity than BA. A similar observation was also reported by Koiry and co-workers [106]. In this case, the copolymerisation of HFBA and BA was carried out in 1,4-dioxane using 4 as the RAFT agent. All the aforementioned studies on the RAFT copolymerisation of FA/FMA displayed an ideal copolymerisation system producing perfectly random copolymers. Zaitsev and co-workers [107] reported the preparation of a fluorinated alternating copolymer from electron-rich *N*-vinylpyrrolidone and electron-deficient 1,1,1,3,3,3-hexafluoroisopropyl (FPFA)- α -fluoroacrylate carried out in THF in the presence of RAFT agent 1.

Most articles have shown that a polymer prepared by RAFT polymerisation usually contains the RAFT functionality as an end-group which can further be used for chain extension reactions to produce block copolymers. Several researchers took this opportunity into account to prepare fluorinated block copolymers with desired architectures. Most of the authors took advantage of the hydrophobic and oleophobic nature of the fluorinated segment to synthesise amphiphilic block copolymers. In this regard, a simple approach was reported by Guo and co-workers [108] who prepared amphiphilic polymethacrylic acid (PMAA)-*b*-PTFEMA *via* RAFT polymerisation in a one-pot process. In this case, the block copolymer was

formed *via* a polymerisation-induced self-assembly process which originated from the water-soluble PMAA macroRAFT agent. Another amphiphilic DBF composed of poly(heptadecafluorodecylacrylate)-*co*-acrylic acid and polyacrylonitrile was prepared by Grignard and co-workers. Electrospinning of the DBF solution in DMF produced a superhydrophobic surface with a WCA up to 155.7° [109]. The RAFT polymerisation process has also been used by Li and co-workers [110] to prepare PMMA-*b*-TFEMA, which displayed significant water- and oil-resistant properties ($\theta_{\text{water}} = 104.3^\circ$ and $\theta_{\text{oil}} = 80.0^\circ$). Due to self-assembly, the DBF displayed micellar aggregates with a diameter of 400–600 nm in aqueous solution. A reactive DBF, PTFEA-*b*-PEGMA, prepared by Yi and co-workers [111] was found to be a promising material for preparing fluorinated thermosets. The amphiphilic DBF was incorporated into epoxy to produce a nanostructured and fluorinated thermoset resin. The material showed a WCA of 102° and surface energy of 16.4 mN/m. Koiry and co-workers [112] used PEG-containing amphiphilic DBF as a surf-RAFT agent (a macroRAFT agent also acting as a surfactant) in the miniemulsion polymerisation of S. In this case, they prepared an amphiphilic PEGMA-*b*-PHFBA using RAFT agent 3. The DBF produced spherical micelles in aqueous solution, which were further used as a polymerisation site for the miniemulsion polymerisation of S producing core-shell particles, where PS occupied the core and DBF was in the shell. Some authors have used the RAFT polymerisation technique to prepare TBF with a hydrophilic-lipophilic-fluorophilic nature [113, 114]. In this case, the authors used the sequential RAFT polymerisation of different monomers along with the fluorinated monomer to demonstrate the triphilic nature of the TBF. Interestingly, the TBF displayed multiple morphologies, such as core-shell-corona micelles and multicompartment micelles, due to their self-aggregation.

6.4.4.1 Reversible Addition-Fragmentation Chain Transfer Polymerisation in Emulsion

Being environmentally friendly, emulsion polymerisation is an extremely important tool for the industrial production of different polymers for paint and coatings purposes, as well as other applications. Since fluorinated polymers have low surface energies, they can be used in paints to improve the water- and oil-resistant properties of the paints or coatings. Researchers have thus incorporated fluorinated segments into polymers synthesised *via* emulsion polymerisation techniques. Thus, the RAFT polymerisation technique has been successfully applied with in emulsion polymerisation processes. However, the extremely hydrophobic nature of the fluorinated monomers has raised issues of colloidal instability. To address this issue, some researchers have adopted miniemulsion polymerisation techniques in combination with the RAFT polymerisation process.

The RAFT miniemulsion polymerisation of HFBA and subsequent chain extension with BA had recently been reported by Chakrabarty and Singha [115]. In this case, PHFBA-*b*-polybutyl acrylate (PBA) displayed core-shell morphology in the miniemulsion phase, where PBA formed the core and PHFBA formed the shell as established by the elemental analysis. This nanophase separation in the DBF, achieved by RAFT-mediated miniemulsion polymerisation, resulted in improved hydrophobicity with a WCA of 112.5°. An interfacial RAFT miniemulsion polymerisation technique was adopted to prepare hollow fluorinated polymer particles [116]. An emulsifier-free method had been used by Chen and co-workers [117] to polymerise TFEMA *via* the RAFT technique. An amphiphilic RAFT agent, produced by the polymerisation of acrylic acid, was used as a stabiliser and macroRAFT agent to produce a fluorinated gradient copolymer. The copolymer underwent self-assembly in different organic solvents. Recently, a similar approach was also adopted by Wang and co-workers [118], who prepared a gradient copolymer of PS and PHFBA.

6.4.4.2 Fluoropolymer Nanocomposites via Reversible Addition-Fragmentation Chain Transfer Polymerisation

Due to the exceptional nature of fluoropolymers, nanocomposites based on fluoro (meth)acrylates result in interesting materials. Due to the high cost of fluoropolymers, incorporation of nanomaterials into the fluoropolymer matrix enables a cost reduction, in addition to improved properties such as resistance to flammability, water and oil. The earlier discussion on siATRP described the preparation of fluoropolymer nanocomposites where the materials exhibited superhydrophobicity. The RAFT polymerisation technique enables surface-initiated reversible addition-fragmentation chain transfer (siRAFT) and surface modification by grafting polymers. Liu and co-workers [119] described a novel approach to modify ramie fibres with PTFEMA *via* RAFT polymerisation. This study revealed the preparation of RAFT functionality on cellulose fibres and subsequent polymerisation of TFEMA in scCO₂. The fluoropolymer-modified fibres displayed excellent hydrophobicity with a WCA up to 149°.

Recently, Yang and co-workers [120] used the siRAFT process to polymerise 1H,1H,2H,2H-heptafluorodecyl acrylate (HFDA) and TFEA from the surface of BaTiO₃. This fluoropolymer/BaTiO₃ nanocomposite was found to be a promising ferroelectric material for energy storage applications. Table 6.2 summarises the literature on the polymerisation of FA/FMA using different RAFT agents.

Chakrabarty and Singha reported the morphology and hydrophobicity of a PHFBA/clay nanocomposite [121]. In this case, the RAFT miniemulsion polymerisation technique was adopted for the *in situ* preparation of the nanocomposite. The addition

of certain comonomers favoured the interactions between PHFBA and the nanoclay. The nanocomposite showed higher surface roughness and a WCA of 128.1°, which is significantly higher than that of the pristine PHFBA.

Table 6.2 Examples of fluoromonomers polymerised using different RAFT agents shown in Scheme 6.24 [101–121]		
RAFT agent used	FA/FMA used	References
1	OFPA, FPFA	[101, 107]
2	HFBA	[115, 121]
3	FHEMA	[104, 112]
4	HFBA, TFEMA, PFPMA	[102, 103, 106, 108]
5	TFEMA, TFEA	[110, 111]
6	TFEMA, HFBA	[117, 118]
7	HFDA, TFEA	[120]
8	DFHA	[116]
9	FDA	[113]
10	FDA	[109]
11	TFEA, PFPA, HFBA	[105]
12	TFEMA	[119]
13	PFBA	[114]
DFHA: Dodecafluoroheptyl acrylate PFBA: 1 <i>H</i> ,1 <i>H</i> -Perfluorobutyl acrylate		

6.4.5 Reverse Iodine Transfer Polymerisation of Fluorinated Acrylates/ Fluorinated Methacrylates

The RITP process is an emerging RDRP technique, as other RDRP methods suffer from certain limitations such as expensive and coloured catalysts (for RAFT and NMP), catalyst removal (for ATRP) and so on. This process can also be applied to polymerise FA/FMA with good results.

Bouilhac and co-workers [122] reported the RITP of FDA in scCO₂. The MW were well controlled for polymerisations with MW targeted in the range of 10–100 kg/mol; however, broad *Đ* (>1.5) were observed. The same team [123] reported the RITP of

FDA initiated by AIBN in trifluorotoluene. The polymerisation took place with very high conversion (>90%); however, the authors did not report the MW and respective $\bar{D}$ values from size exclusion chromatography (SEC) analysis.

6.4.6 Single Electron Transfer–Living Radical Polymerisation of Fluorinated Acrylates/Fluorinated Methacrylates

Single electron transfer–living radical polymerisation (SET–LRP) is a novel method to produce polymers with functional chain ends and controlled MW. The polymerisation is catalysed by Cu(0) in the form of Cu wires, powder, NP and so on. It also requires the presence of nitrogen-containing ligands and polar solvents to stabilise the Cu(II) complex. In this regard, SET–LRP of hydrophilic and hydrophobic acrylates in fluorinated solvents, such as 2,2,2-trifluoroethanol, 2,2,3,3-tetrafluoropropanol were found to be successful, as the solvents contain both hydrophilic and hydrophobic segments [124, 125]. The hydrophilic segment is responsible for the disproportionation of Cu(I), and the hydrophobic segment can solubilise the hydrophobic monomer.

Samanta and co-workers reported the SET–LRP of 1H,1H,2H,2H-perfluorooctyl acrylate (FOA), HFBA, 1H,1H,5H-octafluoropentyl methacrylate (OFPMA) and 1H,1H,5H-OFPA using 2,2,2-trifluoroethanol as the solvent [126]. The polymerisation of FA was carried out at 25 °C, whereas the methacrylates were polymerised at 50 °C. In this case, hydrazine-activated Cu(0) wire was used as the catalyst and Me₆-TREN ‘VIII’ was used as the ligand. SEC analysis showed controlled MW and narrow $\bar{D}$ in all the fluorinated polymers. A ‘thiol–bromo’ click reaction was carried out in the chain end-functionality, which was identified by ¹H-NMR and MALDI-TOF MS analysis.

The same group recently reported the SET–LRP of activated fluoromonomers such as 1,1,1,3,3,3-hexafluoroisopropyl acrylate (HFIA) and 1,1,1,3,3,3-hexafluoropropyl methacrylate using Cu(0) wire as the catalyst, ‘VIII’ as the ligand and 2,2,2-trifluoroethanol as the solvent [127]. In this case, the authors successfully carried out the transesterification reaction with the fluoropolymers containing activated esters using two mild bases, 1,8-diazabicycloundec-7-ene and 1,5,7-triazabicyclo[4.4.0]dec-5-ene. This strategy was found to be an important tool to fabricate complex macromolecular architectures.

6.4.7 Reversible Deactivation Radical Polymerisation of Fluorinated Styrenes

Fluorinated monomers with long perfluoroalkyl side chains (>C₇F₁₅) are toxic, can be bioaccumulated and resistant to degradation [63–65, 128]. Considering them as

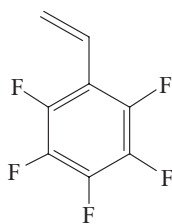
pollutants, The United States Environmental Protection Agency launched its PFOA Stewardship Program to eliminate the production and use of those fluorinated chemicals by 2015. In this regard, monomers bearing fluorinated phenyl rings were found to be a suitable alternative. The polymers derived from these monomers are capable of showing improved surface properties because of their tightly packed structures.

The RDRP of these monomers was successfully carried out to prepare well-defined architectures for many applications in drug delivery, thin-film lithography, anti-biofouling surfaces and so on. **Scheme 6.23** displays the chemical structures of some vinyl monomers containing fluorinated aromatic side groups. Most of these researchers adopted ATRP to polymerise these monomers [16]. In this case, monomer A, the fluorinated analogue of styrene, was found to be widely used and shows a much higher reactivity than styrene during radical polymerisation.

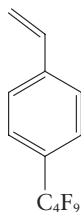
The rate of polymerisation of monomer A was found to be dependent on the nature of the solvent. ATRP in aromatic solvents, like benzene or toluene, produced a higher conversion due to the 'π-π' stacking between the solvent and monomer [129], and this type of interaction increased the stability of the propagating radical. Tan and co-workers [130] prepared an amphiphilic DBF based on monomer A *via* ATRP. The DBF displayed a micellar structure (20–50 nm) in aqueous solution because of the hydrophobicity of the fluorinated aromatic segment.

Fluorinated aromatic rings are prone to nucleophilic substitution reactions because of electron deficiency provided by the electronegative fluorine atoms. An interesting approach to produce monomer 'C' by the derivatisation of monomer 'A' was reported by Dimitrov and co-workers [131]. In this case, the authors carried out nucleophilic substitution of the F atom at the *para*-position of 'A' *via* the hydroxyl group, followed by sulfopropylation to produce 'C' (**Scheme 6.24**). Since the monomer was soluble in water, the ATRP of 'C' followed by chain extension was carried out in a water/methanol (3:1) mixture. The nucleophilic substitution reaction and ATRP process was also adopted by Pollack and co-workers [132] to prepare a well-defined hyperbranched fluoropolymer.

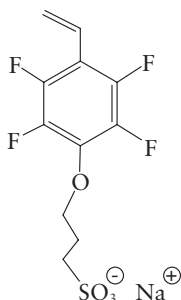
Recent Advances in the Reversible Deactivation Radical (Co)Polymerisation of Fluorinated Alkenes/Acrylates/Methacrylates/Styrenes



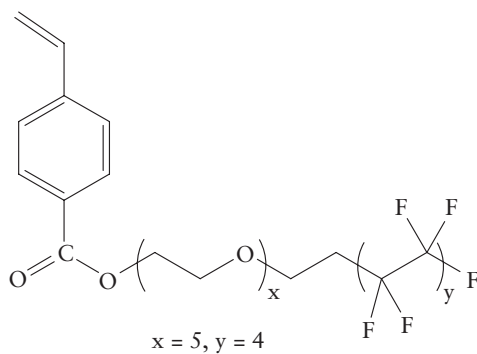
Pentafluorostyrene (A)



4'-Nonafluorobutyl styrene (B)

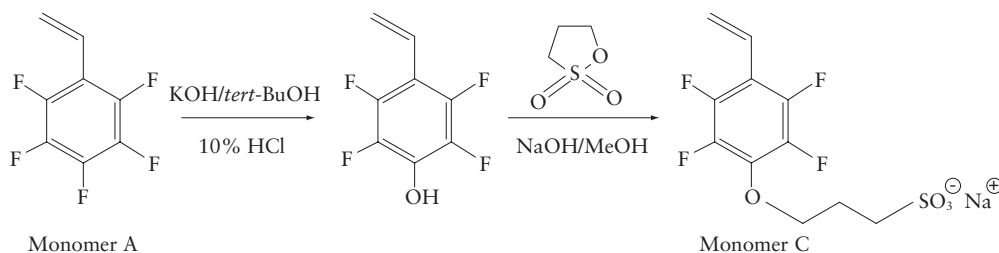


Sodium 3-(2,3,5,6-tetrafluoro-4-vinylphenoxy)propane-1-sulfonate (C)



PEGylated-fluoroalkyl-4-vinylbenzoate (D)

Scheme 6.23 Chemical structures of styrenic monomers bearing fluorinated aromatic rings polymerised *via* the RDRP technique



Scheme 6.24 An approach to derivatise pentafluorostyrene (monomer A). Adapted from I. Dimitrov, K. Jankova and S. Hvilsted, *Journal of Fluorine Chemistry*, 2013, **149**, 30 [131]

Styrenic monomers can also be derivatised by a fluoroalkyl group to prepare fluorinated styrenes. In this regard, Martinelli and co-workers [133] adopted a simple approach by coupling 4-vinylbenzoic acid and a PEGylated-fluoroalkyl surfactant to produce an amphiphilic fluorinated monomer, 'D'. In this case, the ATRP of monomer 'D' using PS-Br as a macroinitiator produced an amphiphilic DBF which displayed considerably lower surface energy due to the formation of a nanostructured surface.

Ceretta and co-workers [134] used another novel approach to prepare monomer 'B', a fluoroalkyl substituted styrene, *via* Ullmann coupling between 1-iodoperfluorobutane and 4-bromoacetophenone followed by a reduction and dehydration. In this case, the authors adopted the ITP technique to achieve narrow *D*. Interestingly, the polymer prepared by ITP displayed higher contact angle hysteresis compared with the same polymer synthesised by conventional radical polymerisation.

6.5 Conclusions and Future Outlook

Due to the nature of F-monomers and their reactivities, specific reactions of RDRP are only suitable for specific monomers. For F-alkenes, ITP, MADIX and reactions involving borane are the most suitable techniques and industrial application of these products as TPE have existed for several decades. As for F-(meth)acrylates and styrenes, ATRP, NMP, RAFT and RITP are the most suitable methods.

Acknowledgements

The authors thank postdoc researchers and PhD students (mentioned as co-authors in the list of references). Industrial companies and colleagues are also thanked for

fruitful discussions and for building valuable collaborations and/or for sponsoring various studies and/or supplying free samples, as well as the French National Agency (ANR, PREMHYS project) and the Council of Scientific and Industrial Research, New Delhi, India for financial support.

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