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**DIRECTED SYNTHESIS OF COPOLYMERS BASED ON FLUORINE-CONTAINING (METH)ACRYLATE DERIVATIVES**

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**Abstract:** The review considers and analyzes the literature data on the directed synthesis of (co)polymers based on fluorine-containing acrylate and methacrylate derivatives, published over the past two decades.

**Keywords:** RAFT-polymerization, copolymers, fluoroacrylates, fluoromethacrylates

**Introduction**

Interest in the directed synthesis of fluorine-containing copolymers is due to their unique properties, such as high thermal and chemical resistance to environmental influences and aging, low values of free surface energy, dielectric constant, refractive index, etc. [1]–[3]. To obtain fluorine-containing copolymers, fluorinated derivatives of (meth)acrylate are most often used because of their high reactivity in polymerization reactions, as well as the convenience and low cost of their synthesis.

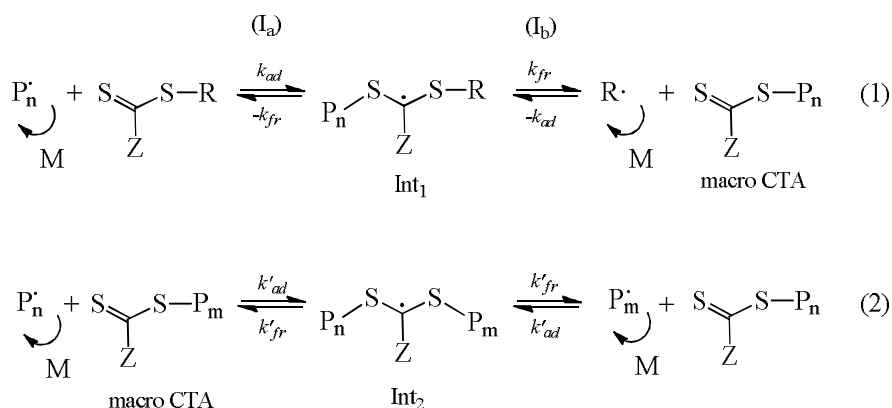
Recently, directed synthesis of fluorinated (co)polymers with the required properties has been carried out by methods of reversible-deactivation radical polymerization (RDRP), such as atom transfer radical polymerization (ATRP), radical polymerization under conditions of reversible inhibition in the presence of nitroxides (nitroxide-mediated polymerization, NMP) and radical addition-fragmentation transfer (RAFT) polymerization [4]–[6]. Of the existing RDRP methods, RAFT polymerization is the simplest and most versatile method for controlled polymer synthesis, since it proceeds under relatively mild conditions and is suitable for a wide range of monomers.

In this review, we will consider in detail the work on RAFT polymerization of fluorinated (meth)acrylates.

### Synthesis of fluorine-containing copolymers by RAFT polymerization

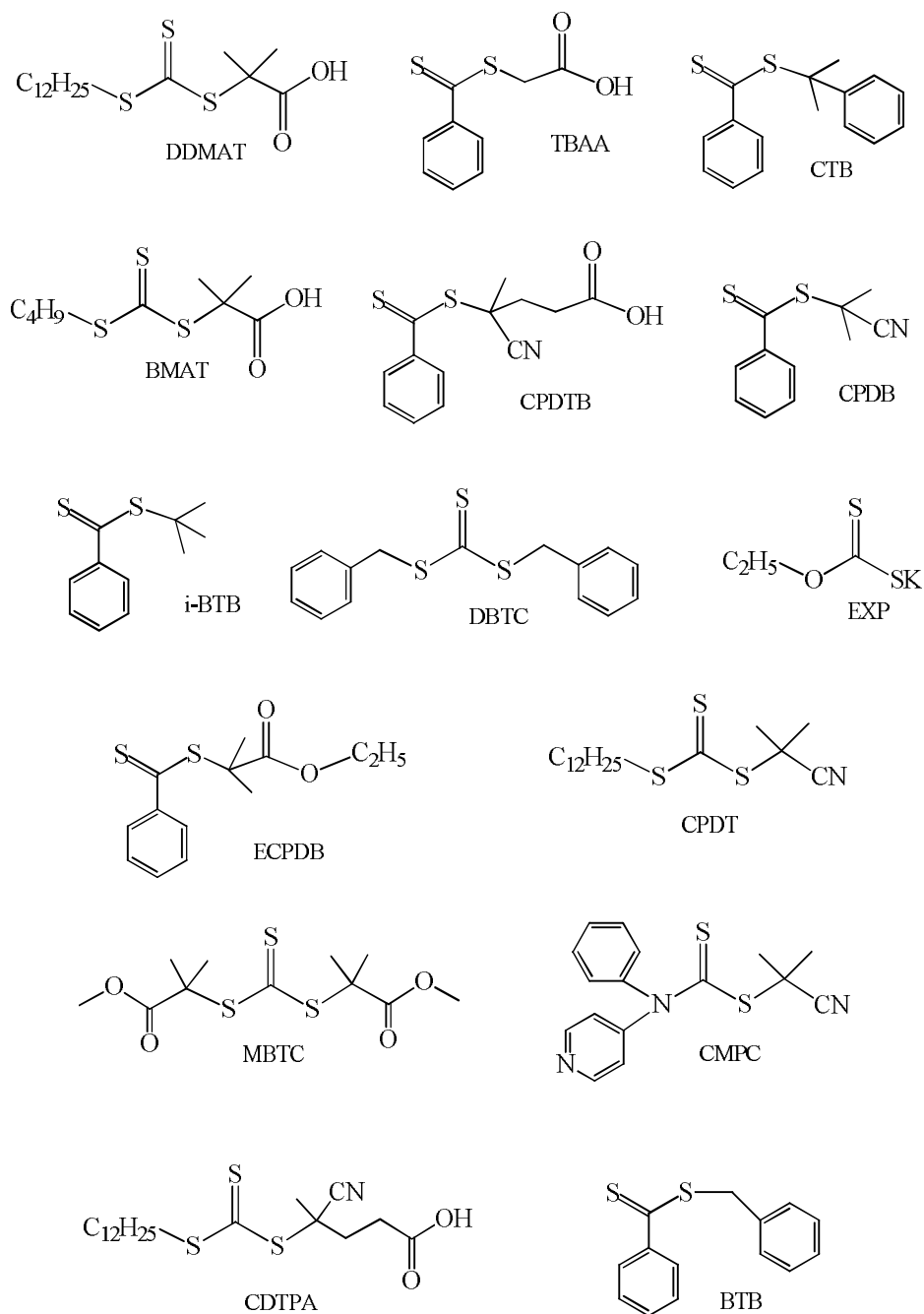
In 1998, the first reports of the Rizzardo group appeared about the use chain transmitters for directed synthesis of polymers – sulfur-containing compounds of general formula  $Z-C(=S)-S-R$ , added to the reaction mixture in catalytic amounts. In the English-language literature, this process is called "reversible addition-fragmentation chain transfer (RAFT-polymerization)" and the chain transmitters are called "chain transfer agent (CTA)" or "RAFT-agent" [7]. In the Russian-language literature the terms "pseudo-living radical polymerization with reversible chain transfer by addition-fragmentation mechanism (RAFT-polymerization)" and "RAFT-agent" are used respectively.

The mechanism of RAFT-polymerization differs from classical radical polymerization by the presence (along with elementary reactions of initiation, growth, termination and chain transfer) stages of the addition of the growing radical to the CTA, followed by fragmentation (decomposition) of the intermediate (Int1 and Int2) and formation of the macroCTA, which further takes part in the process of reversible chain transfer, and growth radical ( $R\cdot$  и  $P_m$ ), which re-initiates polymerization. The scheme of the process is presented below.



**Scheme 1.** Mechanism of RAFT polymerization.

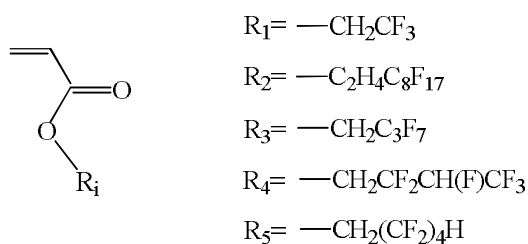
Polymerization control is provided by adding CTA into the system. As a rule, these compounds are classified as dithio- or trithio compounds (Scheme 2). Stabilizing Z- and leaving R-groups have a significant effect on the direction of the polymerization reaction (toward free radical polymerization or toward fragmentation of the intermediate) and on the kinetics of the process. It is important to correctly select the corresponding groups depending on the nature of the monomer used. Below are presented CTAs used in the polymerization of fluorinated (meth)acrylates (Scheme 2).



**Scheme 2.** Examples of CTAs.

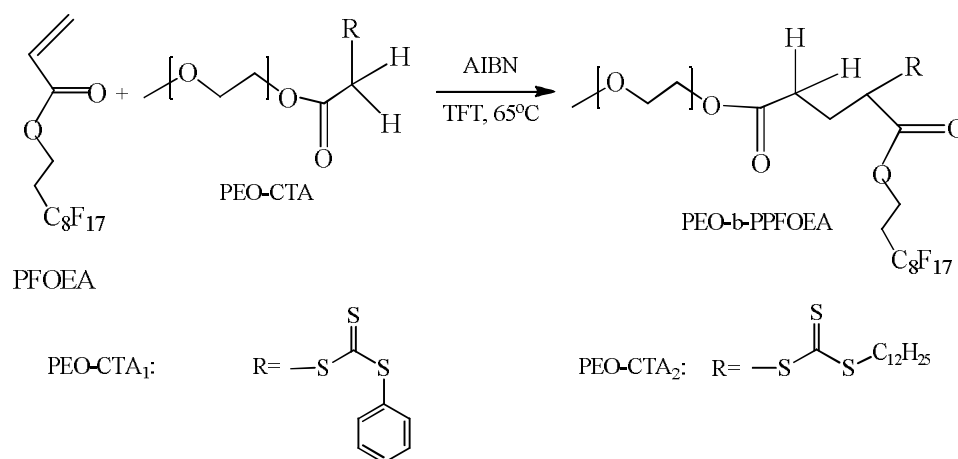
### RAFT polymerization of fluorine-containing acrylates

Works devoted to RAFT polymerization of fluorinated acrylates (Scheme 3) appeared only 6 years later, after the discovery of RAFT polymerization in the presence of thio compounds, and the number of these works is still small [8]-[19].



**Scheme 3.** Examples of fluorine-containing acrylates.

In 2004, Ma et al. performed a detailed study of the RAFT polymerization of perfluorooctylethyl acrylate (PFOEA) in the presence of two CTAs based on polyethylene oxide (PEO) with end-capped groups from 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT) (PEO-CTA<sub>1</sub>) and from thiobenzoylthio acetic acid (TBAA) (PEO-CTA<sub>2</sub>) (Scheme 4) [8]. Polymerization was carried out in trifluorotoluene (TFT) at 65°C with azobisisobutyronitrile (AIBN) as an initiator at molar ratio of [PFOEA] / [CTA] / [AIBN] = 19.32 mmol / 0.537 mmol / 0.108 mmol. In the presence of both CTAs, the reaction proceeded to high conversions (70 and 97.8 % for PEO-CTA<sub>1</sub> and PEO-CTA<sub>2</sub> respectively) without the formation of by-product by uncontrolled radical polymerization of PFOEA. The authors believe that the polymerization has "living" character, since the experimental values of  $M_n$  calculated from the composition of synthesized polymers do not exceed 25 kDa and are in good agreement with the theoretical values.

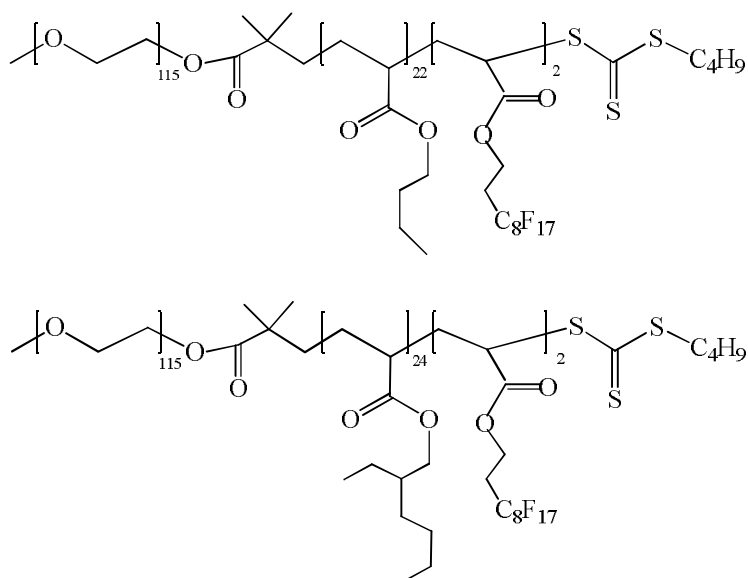


**Scheme 4.** Synthesis of DC (PEO-PPFOEA) [8].

Grignand et al. synthesized amphiphilic random copolymers and diblock copolymers (DC) of PFOEA and 2-hydroxyethyl acrylate (HEA) [9]. The two-stage DC synthesis began with the polymerization of PFOEA in TFT in presence of DDMAT. Copolymers were prepared in a mixed solvent TFT:DMF (1:1 vol.). The study of the kinetics of polymerization by NMR spectroscopy

showed that  $M_n$  values linearly increase with conversion, which, in the authors' opinion, indicates a controlled character of polymerization.

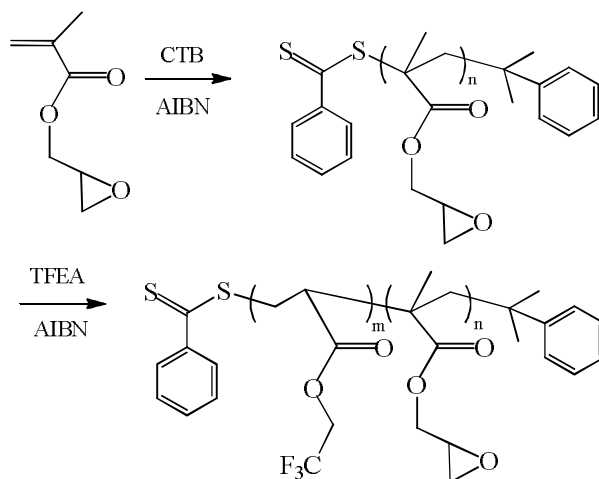
Skrabania et al. [10] reported the preparation of linear amphiphilic triblock copolymers (TC). The authors used a PEO-CTA with a butyl trithiocarbonate end-capped group as the CTA. At the first stage of the synthesis, DC was obtained by polymerizing butyl acrylate (BA) or 2-ethylhexyl acrylate (EHA) in the presence of PEO-CTA, and at the second stage, by polymerizing a fluorine-containing PFOEA in the presence of a diblock copolymer CTA, TC was obtained (Scheme 5).



**Scheme 5.** Synthesis of TC based on PFOEA [10].

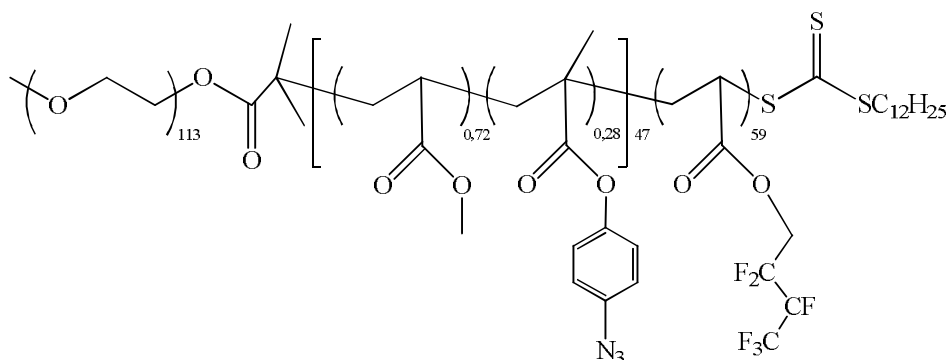
In [11] amphiphilic DCs of 2,2,2-trifluoroethyl acrylate (TFEA) were synthesized by RAFT polymerization of TFEA in the presence of PEO-CTA with a dithiobenzoate end-capped group. The obtained DCs were used as filler for epoxy resin to improve its surface properties. The values of contact angles (CA) for wetting with water (WCA) and ethylene glycol of coatings made of composite thermosets containing 40 wt.% DC dispersed in the epoxy matrix were:  $\theta^{\text{H}_2\text{O}} = 101.2^\circ$  and  $\theta^{\text{C}_2\text{H}_6\text{O}_2} = 84.5^\circ$ , respectively, compared with  $\theta^{\text{H}_2\text{O}} = 74.3^\circ$  and  $\theta^{\text{C}_2\text{H}_6\text{O}_2} = 60.7^\circ$  for the "unfilled" epoxy network. The adding of DCs led not only to an increase in CA, but also decrease in the free surface energy from  $29.4 \text{ mJ/m}^2$  (for epoxy resin) to  $14.9 \text{ mJ/m}^2$  (for a composite). The authors attributed the observed improvement in surface properties to the presence of fluorine atoms ([F] = 6.3 wt. % according to EDS data) on the surface of films made of composite thermosets, which is probably due to the microphase separation of DC in the epoxy matrix. In their other work [12], the authors also achieved an improvement in the surface properties of epoxy network

( $\theta_{\text{H}_2\text{O}}^{\text{H}_2\text{O}} = 102^\circ$  and  $\theta_{\text{C}_2\text{H}_6\text{O}_2}^{\text{C}_2\text{H}_6\text{O}_2} = 83^\circ$ ) and a decrease in the energy characteristics of its surface up to  $16.4 \text{ mJ/m}^2$  due to the adding of DC into epoxy resin obtained by polymerizing TFEA with another comonomer – glycidyl methacrylate (GMA) by using cumyl dithiobenzoate (CTB) as a CTA (Scheme 6).



**Scheme 6.** Synthesis of DC (PGMA-PTFEA) [12].

Li et al. synthesized amphiphilic TC, consisting of polyethylene glycol (PEG) and copolymer block, by copolymerization of methyl acrylate (MA) and 4-azophenylmeth acrylate (APMA), or 2,2,3,4,4,4-hexafluorobutyl acrylate (HFBA) in the presence of PEG-CTA with a terminal dodecyltrithiocarbonate group [13] (Scheme 7).

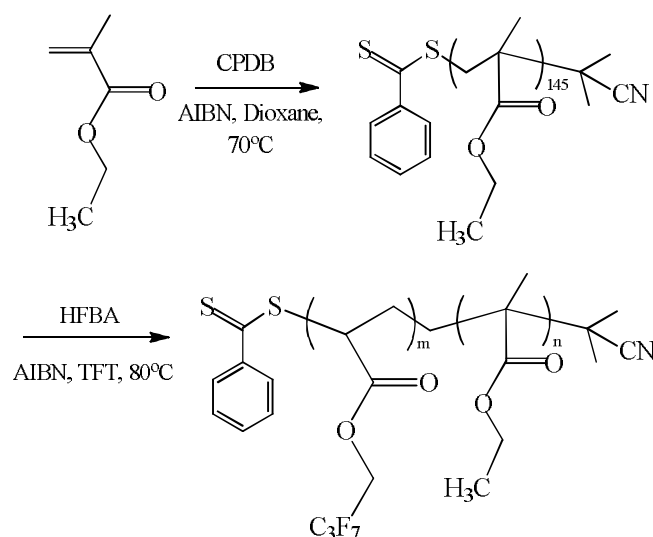


**Scheme 7.** TC (PEG-(MA-co-APMA)-HFBA) [13].

The application of the obtained TC on the hydrophilic cotton fabric transform it into a superhydrophobic material with  $\theta_{\text{H}_2\text{O}}^{\text{H}_2\text{O}} = 155^\circ (> 150^\circ)$  and the value of the CA hysteresis (CAH) =  $2^\circ$  (CAH <  $10^\circ$ ).

In a series of works, Koiry et al. [14]–[16] reported a detailed study of RAFT polymerization of 2,2,3,4,4,4-heptafluorobutyl acrylate (HFBA). In [14], the synthesis of butyl

acrylate (BA) and HFBA copolymers was carried out in the presence 4-cyano-4-((thiobenzoyl)-sulfanyl) pentanoic acid (CPDTB) in dioxane at 90°C. The number average molecular weight of the obtained narrowly dispersed copolymers ( $M_w/M_n = 1.21 \div 1.26$ ), depending on the composition, varies in the range of  $M_n = 16 \div 21$  kDa. In [15], the authors reported on the copolymerization of HFBA with another comonomer methyl methacrylate (MMA) in the presence of 2-cyano-2-propyl dithiobenzoate (CPDB) (Scheme 8).



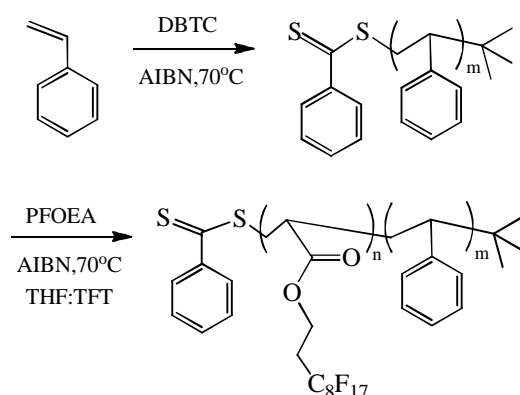
**Scheme 8.** Synthesis of DC (MMA-HFBA) [15].

The ability of the obtained MMA-HFBA copolymers to self-assembly was studied in mixtures of tetrahydrofuran and methyl ethyl ketone (THF-MEK) of various compositions. It is shown that in a mixed solvent THF:MEK = 3:2 copolymers are collected in tubes ( $\lambda \approx 250$  nm). The authors believe that the ability of these DCs to form tubes under the influence of external factors can be used to create self-healing coatings. In [16], amphiphilic DCs of poly(ethylene glycol) methyl ether methacrylate (PEGMA) and HFBA were also synthesized in the presence of CPDB in dioxane at 85°C.

The work [17] describes the preparation of DC by RAFT polymerization of 2-(dimethylamino)ethyl methacrylate DMAEMA and HFBA using CTB as a low molecular weight CTA. Absorbents based on a highly porous material from synthesized DC perfectly absorb oil from aqueous media, while maintaining high values of  $\theta^{H_2O} = 140^\circ$ , even after 3 hours of annealing at 200°C.

The study of the polymerization of PFOEA in the presence of styrene (St) was carried out by Dai et al. [18]. DC synthesis was performed by two-stage RAFT polymerization. At the first stage, polystyrene (PSt) was obtained in the presence of dibenzyl carbonotrithioate (DBTC) in bulk, and at

the second stage, DC was synthesized in a mixture of solvents THF:TFT = 1:1 by volume (Scheme 9).



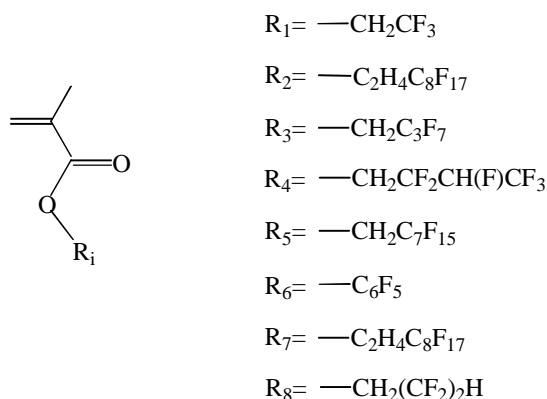
**Scheme 9.** Synthesis of DC (PSt-PPFOEA) [18].

In a recently published paper by Grigoreva et al. [19] considers the RAFT polymerization of 2,2,3,3,4,4,5,5-octofluoropentyl acrylate (OFPA) in the presence of a low molecular CTA DBTC in benzene at 80°C, as well as the copolymerization of OFPA with acrylic acid (AA) and tert-butyl acrylate. The authors were the first to quantitatively characterize the efficiency of DBTC in the polymerization of fluoroacrylate. The criterion for the effectiveness of the CTA is the value of constant of chain transfer to the CTA  $C_{tr}$ . It is conventionally assumed that effective CTA are those for which  $C \gg 1$ . In [19], the  $C_{tr}$  value was determined using the approach described in [20], and it was  $C_{tr} 14 (\gg 1)$ . Under the found conditions, block copolymers with  $M_n = 6.9 \div 95$  kDa and  $M_w/M_n = 1.18 \div 2.85$  and random copolymers with  $M_n = 0.9 \div 63.2$  kDa and  $M_w/M_n = 1.18 \div 5.76$  were obtained. The study of the aggregation behavior of copolymers at the air/water interface by the Langmuir monolayer technique showed that a change in the acidity of the subphase can affect the type of self-organization of macromolecules in the monolayer due to the ionization of carboxyl groups in AA. Under alkaline conditions, the size of micelles increases in comparison with neutral ones and is 90-100 nm.

### RAFT polymerization of fluorine-containing methacrylates

Along with fluorinated acrylates, methacrylates (Scheme 10) are also widely used in the directed synthesis of fluorine-containing block copolymers by RAFT polymerization [21]-[33].





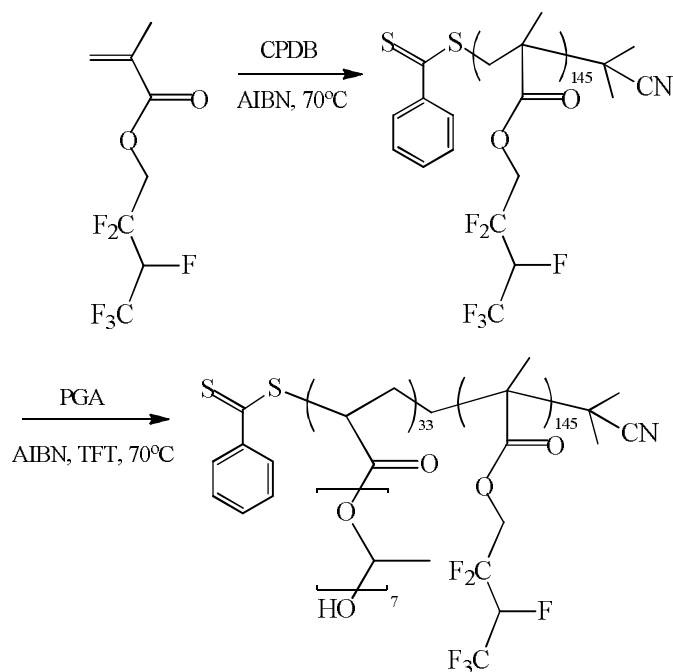
**Scheme 10.** Examples of methacrylate monomers.

In [21], Eberhardt et al. carried out the RAFT polymerization of pentafluorophenyl methacrylate (PFPMA) in the presence of two CTA: CPDTB and CTB. The reaction was carried out in dioxane in the presence of AIBN as initiator. The obtained homopolymers were characterized by low values of the polydispersity index ( $M_w/M_n < 1.3$  for CTB and  $< 1.15$  for CPDTB). Subsequently, amphiphilic DC were obtained by polymerization of MMA, N-acryloylmorpholine (N-AM), and N,N-diethyl acrylamide (DEAA). DC obtained by copolymerization in the presence of CPDTB are characterized by lower polydispersity ( $M_w/M_n < 1.30$ , for DC with  $M_n = 50$  kDa), than DC obtained in the presence of CTB ( $M_w/M_n < 1.40$ ) for DC with lower  $M_n = 20 \div 40$  kDa.

Gradient, statistical and DC of trifluoroethyl methacrylate (TFEMA) and 2-methacryloyloxyethylphosphorylcholine (MPC) were synthesized by RAFT polymerization with CPDTB as a CTA [22]. The presence of hydrophilic and biocompatible MPC units that mimic phospholipids makes these DCs promising for use in biomedicine.

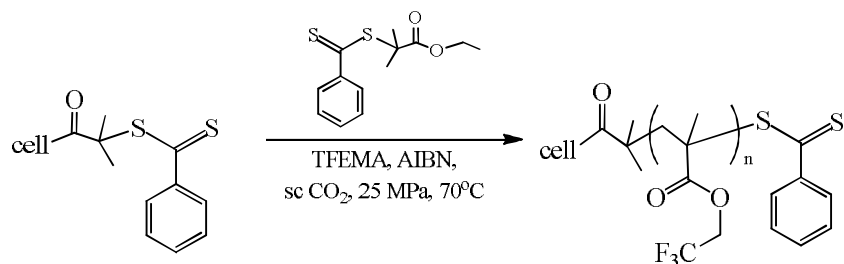
Another article devoted to the study of the surface properties of coatings based on fluorine-containing amphiphilic TC was carried out by Guan et al. [23]. The authors synthesized copolymers based on polydimethylsiloxane, 2,2,3,3,4,4,4-heptafluorobutyl methacrylate and polystyrene (PDMS-HFBMA-PSt). The reaction proceeded in toluene at 60°C, and potassium O-ethylxanthate (EXP) (RAFT/MADIX process) was used as CTA. Films were cast from solutions of the obtained copolymers in THF onto glass substrates. It is shown that, as a result of self-organization, the repellent properties of coatings based on TCs were superior to those for DCs. For example, the WCA for a TC film ( $\theta^{\text{H}_2\text{O}} = 122^\circ$ ) is  $15^\circ$  higher than that for a DC film ( $\theta^{\text{H}_2\text{O}} = 107^\circ$ ). The value of the surface energy for the TC film (10,64 mJ/m<sup>2</sup>), on contrary, is lower than for the DC film (18,72 mJ/m<sup>2</sup>).

Mya et al. investigated the RAFT polymerization of hexafluorobutyl methacrylate (HFBMA) and obtained DC HFBMA and poly(propylene glycol) acrylate (PGA) in the presence of CPDB in TFT [24] (Scheme 11).



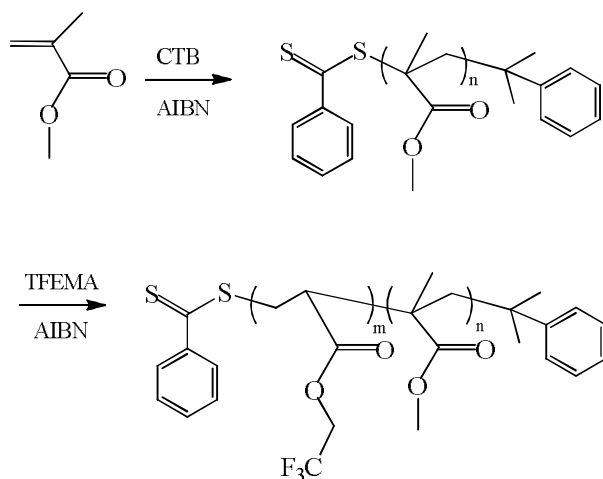
**Scheme 11.** Synthesis of DC (HFBMA-PGA) [24].

Liu et al. [25] hydrophobized ramie fibers by polymerization of TFEMA in supercritical CO<sub>2</sub> in the presence of 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (ECPDB) grafted onto fibers (Scheme 12). After receiving the modified fiber, it is loaded into a CO<sub>2</sub> reactor with a monomer, an initiator, and portion of the "free" CTA. The WCA values of the modified fibers  $\theta_{\text{H}_2\text{O}}^{\text{H}}$  reached 149°.



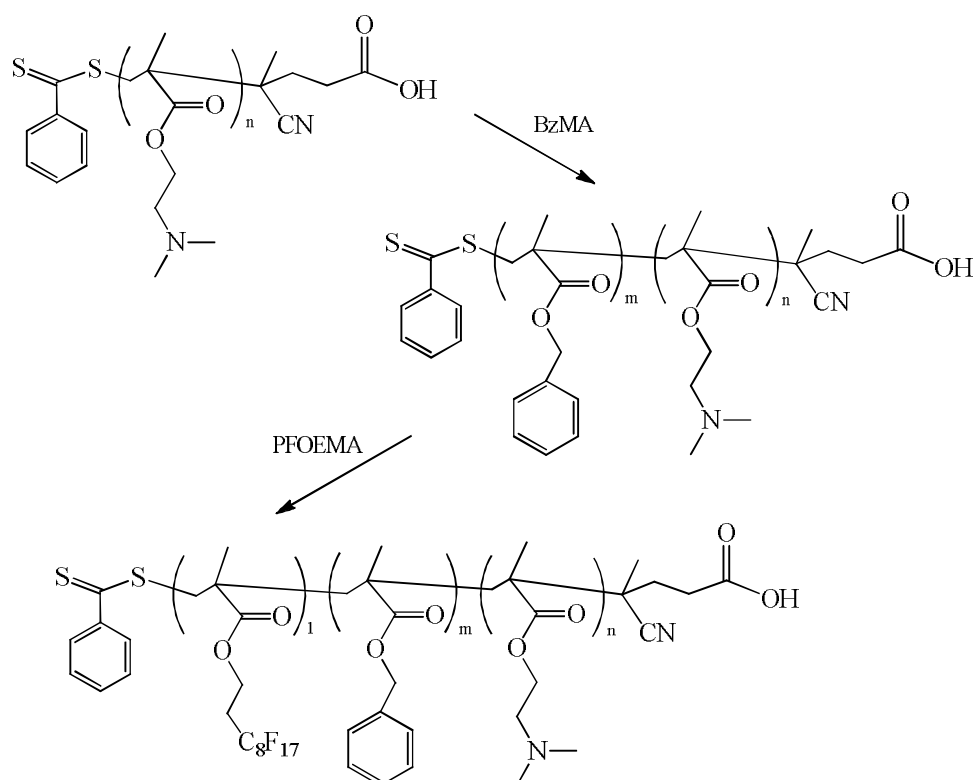
**Scheme 12.** Synthesis of graft copolymer based on TFEMA [25].

Li et al. carried out the synthesis of fluorine-containing DC based on MMA and TFEMA using CTB as CTA [26] (Scheme 13). Films cast from DC solutions in THF onto glass are characterized by increased WCA and CA of ethylene glycol  $\theta_{\text{H}_2\text{O}}^{\text{H}} = 113^\circ$ , a  $\theta_{\text{C}_2\text{H}_6\text{O}_2}^{\text{C}} = 82,4^\circ$ .



**Scheme 13.** Synthesis of DC PMMA-PTFEMA [26].

Huo et al. [27] synthesized amphiphilic TC by polymerizing 2-diethylaminoethyl methacrylate (DEAEMA), benzyl methacrylate (BzMA), and perfluorooctylethyl methacrylate (PFOEMA) in the presence of CPDTB as CTA (Scheme 14), and studied the morphology of multicomponent micelles (MCM) from obtained TC in ethanol solution.

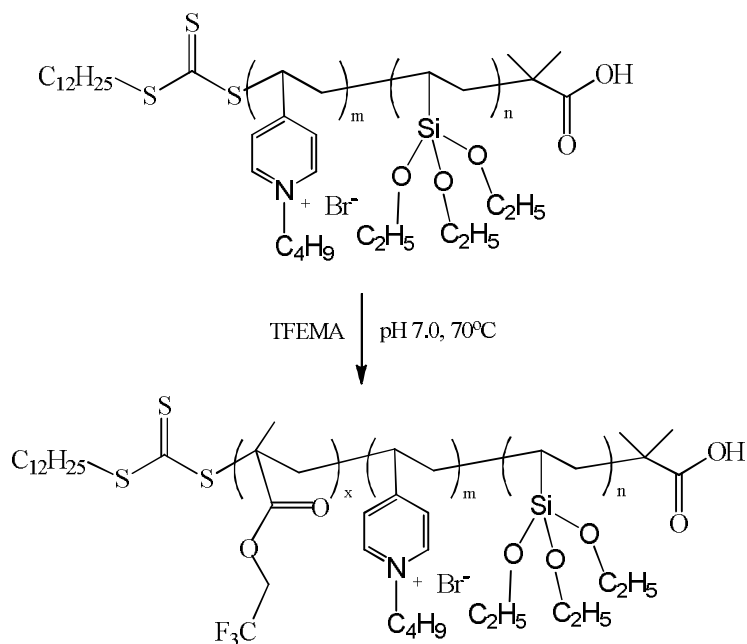


**Scheme 14.** Synthesis of TC (DEAEMA-BzMA-PFOEMA) [27].

The study of the morphology of MCM from TC by TEM showed that with an increase in the mass of the fluorinated block, vesicles from TC are converted first into spheres and then into cylinders.

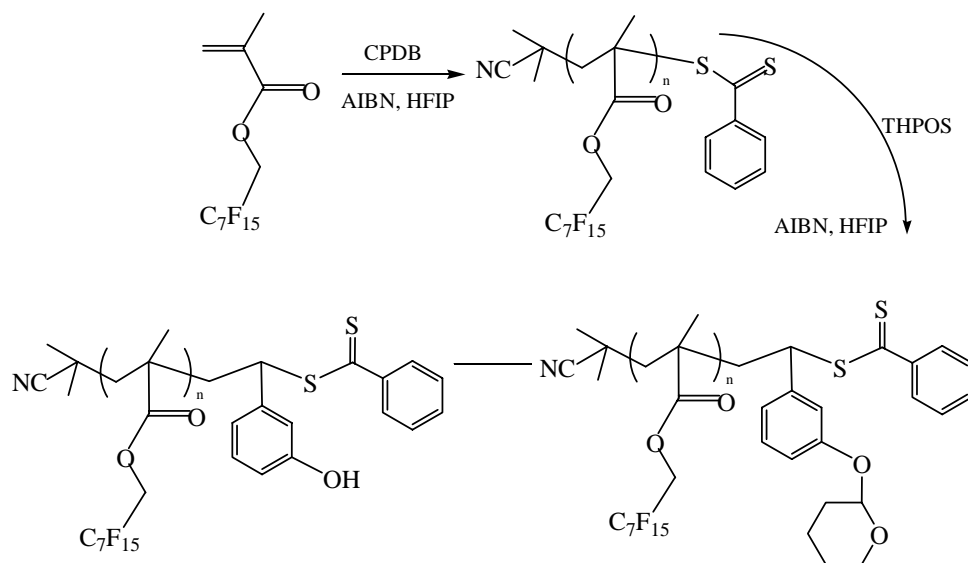
Another work by the same authors [28] reported the preparation of TC by polymerization of DMAEMA with BzMA and perfluorohexylethyl methacrylate (PFHEMA) in the presence of CPDTB.

Not so long ago, Chakrabarti et al. obtained superhydrophobic coatings on glass with  $\theta_{H_2O}$  up to  $151^\circ$  from copolymers of 4-vinyl pyridine and vinyl triethoxysilane with TFEMA obtained by polymerization in the presence of DDMAT [29] (Scheme 15).



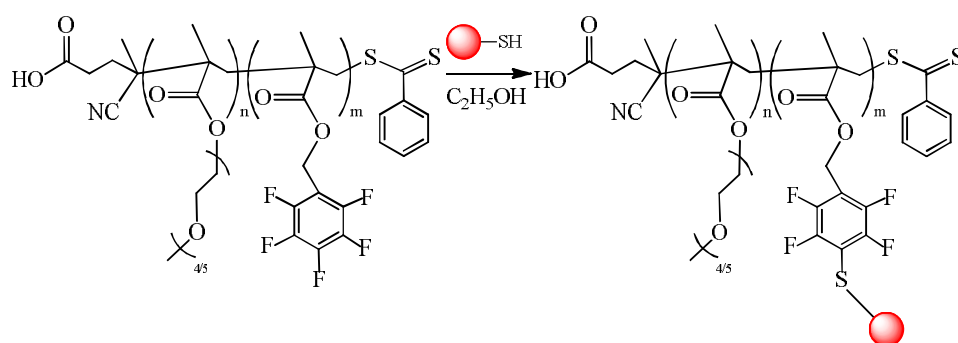
**Scheme 15.** Polymerization of TFEMA in the presence of macroCTA [29].

Wang et al. [30] reported on the preparation of DC based on perfluoroheptylmethyl methacrylate (PFHMMA) and hydroxystyrene (HSt) and on the creation of thin films from the synthesized DCs. Polymerization was carried out in the presence CPDB in hexafluoroisopropanol (HFIP), followed by the removal of the protective tetrahydropyran groups, which prevent side reactions with the participation of hydroxyl groups during polymerization (Scheme 16). The obtained copolymers with a volume fraction of  $f_{HSt} = 0.4 \div 0.69$ , had  $M_n = 2.2 \div 9.5$  kDa and polydispersity  $M_w/M_n = 1.08 \div 1.12$ . The morphology of the films was studied by SAXS and TEM. It is shown that lamellar morphology is characteristic of all DC films. The minimum value of the period of the lamellar structure was 9.8 nm. However, during a short annealing at a moderate temperature ( $80^\circ\text{C}$ , 1 min), the lamellar period decreases to values less than 5 nm.



**Scheme 16.** Synthesis of DC PFHMA-PHSt [30].

The work [31] is devoted to the preparation of DC based on poly[poly(ethylene glycol) methyl ether methacrylate] (PEGMA) and poly(2,3,4,5,6-pentafluorobenzyl methacrylate) (PFBMA) with the subsequent substitution of the fluorine atom in the *para*-position with various thiols (Scheme 17). CPDTB was used as CTA; reaction was carried out in ethanol at 70°C. It was found that DC solutions spontaneously combine to form various nanoparticles, the morphology of which depends on the nature of the substituting thiol and the molecular weight of the copolymer. It was found that the solvophobicity of the nanoparticle core is a more important factor determining morphological transitions compared to the molecular weight of the polymer block that makes up the nanoparticle core.

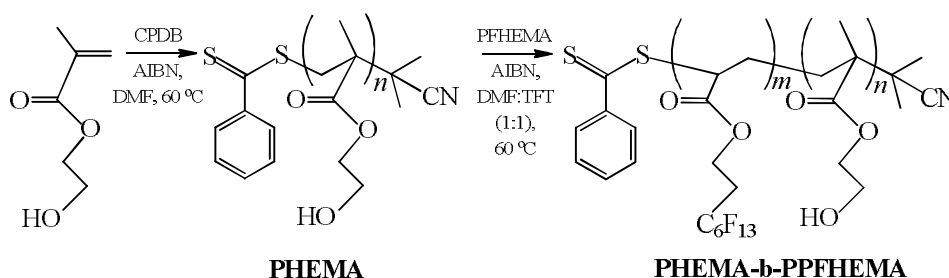


**Scheme 17.** Post-polymerization modification of DC PEGMA-PFBMA with various thiols [31].

Recently Grigoreva et al. published the results of a detailed study of RAFT polymerization of 2,2,3,3-tetrafluoropropyl methacrylate (TFPMA) in the presence of both low molecular CTAs (such as DDMAT, DBTC, 2-cyano-2-propyldodecyl trithiocarbonate (CPDT), S,S'-bis(methyl-2-isobutyrate)trithiocarbonate (MBTC), 1-cyano-1-methylethylphenyl(4-pyridinyl)dithiocarbamate

(CMPC), 4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CDTPA), Dibenzyl carbonotrithioate (BTC)) and macroCTAs based on AA, methacrylic acid (MAA) and GMA [32]. For two CTAs (CPDT and CDTPA), the values of the chain transfer constants ( $C_{tr}$ ) were determined; their values were 1.6 and 3.2 respectively. The obtained amphiphilic DCs based on macroCTAs had  $M_n = 8 \div 45$  kDa and polydispersity  $M_w/M_n = 1.08 \div 1.31$ .

Not so long ago, we synthesized DC based on 2-hydroxyethyl methacrylate (HEMA) and PFHEMA in the presence of low molecular weight CPDB in DMF at 60°C (Scheme 18) and studied the surface properties of DC coatings on cotton fabric depending on the DC composition [33]. It was found that the transformation of hydrophobic coatings into superhydrophobic ones is determined by the composition of the DC and occurs when the ratio of lengths of the PHEMA and PPFHEMA blocks  $P_n^{PHEMA} / P_n^{PPFHEMA} = 15.12$ . The maximum improved surface properties are observed when applied to cotton fabric DC with composition of PHEMA:PPFHEMA = 6:94 mol.%; WCA and CA of diiodomethane  $\theta^{H_2O} = 152 \pm 2^\circ$  and  $\theta^{CH_2I_2} = 120 \pm 3^\circ$ , and these indicators practically do not change after repeated washing with washing powder at a temperature of 40°C for 45 min.



**Scheme 18.** Synthesis of DC PHEMA-b-PPFHEMA [33].

## Conclusion

It can be seen from the presented review that over the past decade, thanks to the use of the RAFT polymerization method, significant progress has been made in the directed synthesis of new (co)polymers based on fluorinated (meth)acrylate to create materials with unique properties, in particular, superhydrophobic coatings of various surfaces.

## Acknowledgments

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