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α-Fluoroacrylates: synthesis, properties and use

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ABSTRACT. Studies on the synthesis and properties of a new class of monomers—α-fluoroacrylic acid derivatives—are reviewed. Promising areas for the application of synthetic polymeric materials based on α-fluoroacrylates are examined.

The bibliography includes 115 references.

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I. Introduction

Polymers based on acrylates are of fundamental importance in current engineering and technology. In this class of polymers a special position is occupied by poly(methyl methacrylate)—a transparent, impact-resistant, heat-resistant material used in optics. It was known even at the beginning of the 1950's that poly(methyl α-fluoroacrylate) is considerably superior to poly(methyl methacrylate) as regards its physicomechanical properties. However, at that time methods had not been developed for the synthesis of α-fluoroacrylates, which would have provided the opportunity for an extensive study of the properties of materials based on monomers of this class. Research into convenient methods for the synthesis of α-fluoroacrylic acid and its derivatives was systematically conducted in many developed countries of the world during recent decades but it was only in the 1980's that the results of comprehensive studies on poly(α-fluoroacrylates) were published, specifying potential areas of application of these fluoropolymers.

In the present article we review the published studies on α-fluoroacrylates and their polymers with the aim not only of demonstrating the existing progress in this field of chemistry but also of determining the direction of studies that could lead to the very rapid practical application of these excellent synthetic materials.

II. Methods of synthesis of α-fluoroacrylic acid and its derivatives

1. Methods based on condensation reactions of derivatives of fluoroacetic and fluoromalonic acids with carbonyl compounds

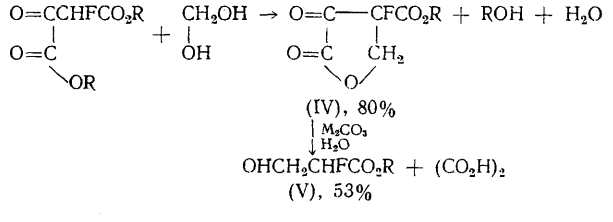
Until recently one of the most widely used methods for the synthesis of α-fluoroacrylates was a method based on a crossed Claisen condensation of alkyl monofluoroacetates with esters of formic and oxalic acid in the presence of strong bases.

The reaction is usually carried out in a solvent (tetrahydrofuran, ether, benzene, methylene chloride) and alkali metal hydrides and alkoxides are used as bases. It is assumed that at the first stage of this reaction nucleophilic addition of a carbanion from fluoroacetate (I) to ester (II) takes place, giving a formyl-, monofluoroacetyl- or oxalyl-acetate (III a–c).[1–5]

$$\underset{\text{(I)}}{CH_2FCO_2R} + \underset{\text{(II)}}{R'CO_2R} \xrightarrow{ROM} \underset{\text{(IIIa–c)}}{R'COCHFCO_2R}$$

R′ = H (a), CH_2F (b), CO_2R (c); R = alkyl (C_{1-7}); M = Li, Na, K.

The majority of the studies in which reproducible results on the synthesis of α-fluoroacrylates have been obtained are based on the use of oxalylfluoroacetates (III c),[6–9] which are condensed with paraformaldehyde to give a lactone (IV). In two studies[6,7] this lactone (IV), R = Et, was isolated and characterised.



Hydrolysis of lactone (IV) in the presence of weak bases (alkali metal carbonates or bicarbonates) gives 2-fluoro-3-hydroxyesters (V).[6–11]

In certain patents the conversion of esters (V) to α-fluoroacrylates (VI) is effected by dehydration.[12,13]

$$\underset{\text{(V)}}{OHCH_2CHFCO_2R} \xrightarrow[-H_2O]{} \underset{\text{(VI)}}{CH_2{=}CFCO_2R}.$$

2-Fluoro-3-hydroxyesters (V) can be converted to esters of 2-fluoro-3-halopropionic acids (VII) by treating them with thionyl chloride or phosphorus tribromide in the presence of pyridine.[14] When treated with bases (hydroxides of alkali and alkaline

earth metals, ammonia, primary, secondary, and tertiary amines), esters (VII) readily eliminate a hydrogen halide to form α-fluoroacrylates (VI).[15,16]

$$\underset{\text{(V)}}{OHCH_2CHFCO_2R} \xrightarrow[C_5H_5N]{SOCl_2(PBr_3)} \underset{\text{(VII)}}{HalCH_2CHFCO_2R} \xrightarrow{\text{base}} \underset{\text{(VI)}}{CH_2{=}CFCO_2R}.$$

Methods for converting esters (V) to the tosyloxy derivatives (VIII) by treating them with *p*-toluenesulphonyl chloride have been reported.[10,11]

$$HOCH_2CHFCO_2R + p\text{-}CH_3C_6H_4SO_2Cl \xrightarrow{C_5H_5N} \rightarrow p\text{-}CH_3C_6H_4SO_2OCH_2CHFCO_2R \xrightarrow[\text{99\%}]{K_2CO_3,\ \text{60\%}} CH_2{=}CFCO_2R.$$

(VIII) (VI)

It is also possible to obtain α-fluoroacrylamide by using 2-fluoro-3-tosyloxy derivatives (VIII). In order to achieve this, ester (V) after treatment with ammonia gives 2-fluoro-3-hydroxypropionamide (IX), which is converted to the tosyloxy derivative (X). α-Fluoroacrylamide (XI) is obtained by treating tosylate (X) with sodium methoxide or potassium phthalimide.[10,11]

By dehydrating amide (X) with thionyl chloride in dimethylformamide or trifluoroacetic anhydride it is possible to obtain 2-fluoro-3-tosyloxypropionitrile (XII),[17,18] treatment of which with potassium phthalimide gives α-fluoroacrylonitrile (XIII).

$$\underset{\text{(V)}}{HOCH_2CHFCO_2R} \xrightarrow{NH_3} \underset{\text{(IX), 100\%}}{HOCH_2CHFCO_2NH_2} \xrightarrow[C_5H_5N]{p\text{-}CH_3C_6H_4SO_2Cl} \rightarrow \underset{\text{(X), 92\%}}{p\text{-}CH_3C_6H_4SO_2OCH_2CHFCONH_2} \xrightarrow{\text{base}} \underset{\text{(XI)}}{CH_2{=}CFCONH_2}$$

$$\xrightarrow[DMF]{SOCl_2} \underset{\text{(XII)}}{p\text{-}CH_3C_6H_4SO_2OCH_2CHFCN} \xrightarrow[\text{90\%}]{(CF_3CO)_2O} \underset{\text{(XIII), 70\%}}{CH_2{=}CFCN}$$

Nitrile (XIII) can be obtained directly by dehydration of α-fluoroacrylamide (XI) with phosphorus pentoxide, but the yield of nitrile using this method is considerably lower.[9,10]

The synthesis of aryl α-fluoroacrylates based on lactone (IV) is carried out via the isolation of a salt of α-fluoroacrylic acid (XIV).[20,21] This is because in lactone (IV) R can only be an alkyl group and not an aryl group, since alkali metal phenolates are not sufficiently strong bases to be able to initiate the Claisen reaction in the synthesis of lactone (IV). Salt (XIV) is converted to α-fluoroacrylyl chloride (XV) by treatment with benzoyl chloride[11] or with thionyl chloride.[20,21] Reaction of acid chloride (XV) with phenol using trimethylamine as an acceptor of HCl gives phenyl α-fluoroacrylate (VIb). The yield of crude product calculated on the basis of monofluoroacetate (I) is 60% of theoretical.

$$\underset{\text{(IV)}}{O{=}C{<}\begin{matrix}CFCO_2Et\\ CH_2\end{matrix}{>}O} + NaOH \xrightarrow[-(CO_2H)_2]{} \underset{\text{(XIV)}}{CH_2{=}CFCO_2Na} \xrightarrow[PhCOCl]{SOCl_2,\ 160^\circ C} \rightarrow \underset{\text{(XV)}}{CH_2{=}CFCOCl} \xrightarrow{PhOH,\ Et_3N} \underset{\text{(VIb)}}{CH_2{=}CFCO_2Ph},$$

The nucleophilic addition of dialkyl fluoromalonates to formaldehyde in the presence of bases (piperidine, alkali metal carbonates and bicarbonates) has recently begun to be used for the synthesis of α-fluoroacrylate esters.[19,22–27]

The primary products of this reaction are dialkyl α-fluoro-α-hydroxymethylmalonates (XVI). Esters (XVI) are hydrolysed and decarboxylated in an acidic medium at elevated temperatures. The resulting acid (XVII) is converted to its ammonium salt, and aryl and alkyl α-fluoroacrylates are then obtained by the usual methods (VI).

$$\begin{matrix}CO_2R\\ CHF\\ CO_2R\end{matrix} + CH_2O \xrightarrow{KHCO_3,\ H_2O} \underset{\text{(XVI)}}{\begin{matrix}CO_2R\\ FC{-}CH_2OH\\ CO_2R\end{matrix}} \xrightarrow[100^\circ C]{HCl} \rightarrow \underset{\text{(XVII)}}{[CH_2{=}CFCO_2H]} \xrightarrow{NH_3} CH_2{=}CFCO_2NH_4.$$

The yield of α-fluoromalonates (VI) does not exceed 50% calculated on the basis of fluoromalonates.

2. Methods based on the reactions of conjugated halofluorination of propene compounds

Since the discovery by Bowers of the method of conjugated halofluorination of unsaturated compounds with *N*-haloamides in anhydrous hydrogen fluoride,[28,29] certain research workers have investigated ways of introducing fluorine into the α-position relative to the carbonyl group.[30–33]

As expected, electrophilic halofluorination of methyl acrylate with *N*-haloamides (*N*-bromoacetamide, 1,3-dibromo-5,5-dimethylhydantoin, hexachloromelamine) in HF gives 3-fluoro-2-halopropionates in moderate yield, regardless of the type of solvent added or reaction temperature (in the range 0 to −78 °C):

$$CH_2{=}CHCO_2Me \xrightarrow[HF]{>N-Hal} \underset{\text{30—50\%}}{CH_2FCHHalCO_2Me}$$

2-fluoro-3-halopropionates are only formed in these reactions in small quantities.[33,34] The synthesis of the precursors of α-fluoroacrylates — 2-fluoro-3-halopropionates — is achieved by halofluorination of allyl alcohol, allyl acetate, allyl trichloroacetate.[33,35] The chlorofluorination of allyl alcohol with hexachloromelamine and anhydrous HF in methanol has been studied in the greatest detail.[35,36] Even under optimum conditions for this reaction the yield of 2-fluoro-3-chloropropanol (XVIII) does not exceed 50%. The reaction is accompanied by a large number of side reactions — the formation of isomeric fluorochloropropanol

(XIX), methoxychloro- and dichloro-propanols, and also the oxidation of allyl alcohol to acrolein:

$$CH_2{=}CHCH_2OH \xrightarrow[MeOH,CHCl_3,0°C]{NCl_3,HF} CH_2ClCHFCH_2OH + \underset{(XVIII),\ 45-47\%}{}$$

$$+ CH_2FCHClCH_2OH + CH_3OCH_2CHClCH_2OH +$$
$$(XIX),\ 5-6\% \qquad 9-10\%$$

$$+ CH_2ClCHCH_2OH + CH_2{=}CHCHOCH_3$$
$$\quad OCH_3 \qquad\qquad OH$$
$$5-6\% \qquad 18-25\%$$

Chlorofluoropropanol (XVIII) that is isolated is oxidised in high yield by nitric acid to give 2-fluoro-3-chloropropionic acid (XX), which after dehydrochlorination with a solution of NaOH in methanol and acidification gives α-fluoroacrylic acid (XVII):

$$CH_2ClCHFCH_2OH \xrightarrow[80-100°C]{HNO_3} CH_2ClCHFCO_2H \xrightarrow[2)\ H_2SO_4]{1)\ NaOH}$$
$$(XX),\ 88\%$$

$$\longrightarrow CH_2{=}CFCO_2H.$$
$$(XVII),\ 60\%$$

Attempts to improve the yield of 2-fluoro-3-chloropropanol (XVIII) by protecting the hydroxyl group of allyl alcohol from being oxidised to acrolein (chlorofluorination of allyl acetate, allyl trichloroacetate and allyl trifluoroacetate) did not produce the desired result,[36] since the yield of the isomeric chlorofluoropropanol (XIX) increased significantly. The presence of this alcohol in 2-fluoro-3-chloropropanol (XVIII) during the subsequent oxidation and dehydrohalogenation gives rise to an impurity that is difficult to separate — α-chloroacrylic acid.[35]

3. Methods based on the fluorination of propene and halopropane derivatives with halogen fluorides

The first attempts to use bromine trifluoride for the synthesis of α-fluoroacrylates were undertaken by Yakubovich et al.[37] Reaction of methyl acrylate with BrF_3 (molar ratio of acrylate to BrF_3 = 2:1) in freon-113 gave a mixture of dihalopropionates with a total yield of 63%:

$$CH_2{=}CHCO_2Me \xrightarrow[freon\text{-}113,0\ °C]{BrF_3} CH_2FCHFCO_2Me +$$
$$19\%$$
$$+ CH_2BrCHFCO_2Me + CH_2FCHBrCO_2Me.$$
$$13\% \qquad 31\%$$

Methyl α-fluoroacrylate was obtained in low yield from this mixture by dehydrohalogenation with triethylamine.

The preparative possibilities of using halogen fluorides for this purpose were investigated again subsequently.[38-42]

The chlorofluorination of methyl methacrylate and allylic esters with a stoichiometric quantity of chlorine monofluoride in inert solvents ($CHCl_3$, CCl_4, CCl_2FCClF_2) has been studied.[38] Under these conditions ClF readily adds to the C=C bonds of these unsaturated esters, although the yield of the α-fluoroacrylate precursors — esters (XXI) and (XXIII a–c) — does not exceed 50% because of the lack of regiospecificity in addition:

$$CH_2{=}CHCO_2Me \xrightarrow[CHCl_3,\ 25°C]{ClF} CH_2ClCHFCO_2Me + CH_2FCHClCO_2Me,$$
$$(XXI),\ 28\% \qquad (XXII),\ 61\%$$

$$CH_2{=}CHCH_2OC(O)R \xrightarrow{ClF} CH_2ClCHFCH_2OC(O)R +$$
$$(XXIIIa-c)$$
$$R_a = H\ 30\%$$
$$R_b = CH_3\ 42\%$$
$$R_c = CCl_3\ 50\%$$
$$+ CH_2FCHClCH_2OC(O)R.$$
$$(XXIVa-c)$$
$$18\%$$
$$28\%$$
$$32\%$$

The use of HF as the medium for chlorofluorination in the case of allylic derivatives does not improve the yield of the required regioisomers (XXIII a–c), while for methyl methacrylate the yield of isomer (XXI) is sharply reduced.[36]

The ability of halogen fluorides to replace a bromine atom on saturated carbon by a fluorine atom is utilised for the synthesis of α-fluoroacrylic acid derivatives.[39-43] In a number of cases this reaction is more selective than addition to a multiple bond. Starting from 1,2-dibromo-3-chloropropane (XXV), which is obtained in quantitative yield by bromination of allyl chloride, methods for the synthesis of two key fluorinated compounds — 1-bromo-2-fluoro-3-chloropropane (XXVI) and 1,2-difluoro-3-chloro-propane (XXVIII) — have been developed.[43]

$$CH_2BrCHBrCH_2Cl\ (XXV) \xrightarrow{1/3BrF_3} CH_2BrCHFCH_2Cl + CH_2FCHBrCH_2Cl$$
$$(XXVI),\ 60\% \qquad (XXVII),\ 25\%$$
$$CH_2BrCHBrCH_2Cl\ (XXV) \xrightarrow{2/3BrF_3} CH_2FCHFCH_2Cl$$
$$(XXVIII),\ 85\%$$

Bromofluorochloropropane (XXVI) is readily separated from its isomer (XXVII). Reaction of (XXVI) with potassium acetate in dimethylformamide in the presence of the phase-transfer catalyst triethylbenzylammonium chloride gives 2-fluoro-3-chloropropyl acetate (XXIX) in good yield. Acetate (XXIX) is readily and in high yield oxidised by nitric acid to 2-fluoro-3-chloropropionic acid (XX), and the latter reacts with thionyl chloride to give the corresponding acid chloride (XXX). In the presence of a catalytic quantity of tertiary amines acid chloride (XXX) gives α-fluoroacrylyl chloride (XV) in high yield.

$$CH_2ClCHFCH_2Br\ (XXVI) \xrightarrow[DMF]{AcOK,\ 80°C} CH_2ClCHFCH_2OAc\ (XXIX),\ 75\% \xrightarrow{HNO_3,\ 80-100°C}$$
$$\rightarrow CH_2ClCHFCO_2H\ (XX),\ 85\% \xrightarrow[80-100°C]{SOCl_2} CH_2ClCHFCOCl\ (XXX),\ 90\% \xrightarrow[100-130°C]{R_3N(5\%)} CH_2{=}CFCOCl.\ (XV),\ 90\%$$

High yields of alkyl, fluoroalkyl, aryl, and organophosphorus esters of α-fluoroacrylic acid are obtained by traditional methods from acid chloride (XV).[43-45] α-Fluoroacrylyl fluoride (XXXI) is obtained in a similar manner from difluorochloropropane (XXVIII).

These methods are multistage and the yield of α-fluoroacrylates based on dibromochloropropane does not exceed 35%, but the degree of purity of the monomers obtained in this way is very high.

Methyl α-fluoroacrylate (VIc) can be obtained by a simpler method — from methyl 2,3-dibromo-2-chloropropionate (XXXII).[43]

$$CH_2BrCClBrCO_2Me \xrightarrow[\text{freon-113}]{1/3BrF_3} CH_2BrCClFCO_2Me \rightarrow$$
(XXXII) 85%

$$\xrightarrow[H_2O]{Zn,H^+,100^\circ C} CH_2{=}CFCO_2Me$$
(VI в), 85%

α-Fluoroacrylonitrile (XIII) is readily obtained from 2-fluoro-3-chloropropionyl chloride (XXX):

$$CH_2ClCHFCOCl \xrightarrow{MeOH} CH_2ClCHFCO_2Me \xrightarrow{NH_3} CH_2ClCHFCONH_2 \rightarrow$$
(XXX) (XXI), 95% 90%

$$\rightarrow \xrightarrow[180-250^\circ C]{P_2O_5} CH_2ClCHFCN \xrightarrow{base} CH_2{=}CFCN.$$
70% (XIII), 85%

4. Other methods for the synthesis of α-fluoroacrylates

The most recent method for the synthesis of α-fluoroacrylates is based on the substitution of organobromine derivatives by mercuric fluoride followed by dehalogenation of the fluorine derivative with zinc dust.[46–49] The corresponding esters are formed in very low yield (5–15%).

$$CH_2{=}CHCO_2R \xrightarrow{Br_2} CH_2BrCHBrCO_2R \xrightarrow{\text{quinoline}} CH_2{=}CBrCO_2R \rightarrow$$
$$\xrightarrow{Br_2} CH_2BrCBr_2CO_2R \xrightarrow{HgF_2} CH_2BrCBrFCO_2R \xrightarrow[Et_2O]{Zn} CH_2{=}CFCO_2R.$$

Fluoroalkyl α-fluoroacrylates can be obtained in a similar manner from the corresponding acrylate analogues.[50]

The Prince reaction was used in a number of studies for the synthesis of different α-fluoro-substituted propionic acids.[12,13,15,51,52] For example, the condensation of paraformaldehyde with 1,2-difluoro-1,2-dichloroethylene, which takes place most effectively in chlorosulphonic or fluorosulphonic acid, gives the α-fluoroacrylate precursors (XXXIII) and (XXXIV).

$$CClF{=}CClF + CH_2O \begin{cases} \xrightarrow[2)\ HCl,KCl]{1)\ ClOSO_2H} HOCH_2CFClCO_2H \\ \text{(XXXIII), 45—50\%} \\ \xrightarrow[2)\ HCl,KCl]{1)\ FOSO_2H} HalCH_2CClFCO_2H \\ \text{(XXXIV), 45—50\%} \end{cases}$$

The condensation of paraformaldehyde with trifluoroethylene occurs under similar conditions, giving 2-fluoro-3-hydroxypropionic and 2-fluoro-3-halopropionic acids.[13,15] Alkyl α-fluoroacrylates are obtained from these acids by various methods, as described in the previous sections.[12–17]

Subsequent studies on the possibility of using the Prince reaction for the synthesis of α-fluoroacrylates resulted in the development of a new starting compound for this purpose — 2,2,3,3-tetrafluoroxetane (XXXV).[53–57]

$$CF_2{=}CF_2 + CH_2O \xrightarrow[8\ atm]{HF,80^\circ C} \underset{\text{(XXXV), 17\%}}{\overset{CF_2-CF_2}{\underset{CH_2-O}{|\quad|}}} \xrightarrow[DMF]{ROH,NaI,Zn,60^\circ C} CH_2{=}CFCO_2R.$$
(VII), 50—80%

Reaction of tetrafluoroxetane, alkali metal halides, and a dehalogenating agent (molar ratio of 1 : 0.1–1.5 : 0.3–3 respectively) in aprotic bipolar solvents in the presence of a radical polymerisation inhibitor gave α-fluoroacrylyl fluoride (XXXI), which was converted to esters by reaction with the respective alcohols.[55–57] According to the information from patents, the esters can be prepared in one stage without isolation of the acid fluoride. Thus, methyl α-fluoro-deuteroacrylate with a yield of 76% based on oxetane (XXXV) was also obtained by this method.[55]

Original methods for the synthesis of α-fluoroacrylates are based on the addition of chlorofluorocarbene to vinyl ethers.[58–64] Thus, the large-scale synthesis of one of the precursors of α-fluoroacrylates — 2-fluoroacrolein (XXXIX) — has been reported by Molines et al.[58]

$$CH_2{=}CHOR + CHFCl_2 \xrightarrow[Et_4NBr,5^\circ C]{NaOH,CH_2Cl_2,H_2O} \rightarrow$$
$R = n\text{-}C_4H_9$

$$\rightarrow \underset{\text{(XXXVI), 79\%}}{CH_2-\overset{Cl}{\overset{|}{C}}(F)-CHOR} \xrightarrow{C_5H_5N} \underset{\text{(XXXVII)}}{\left[CH_2{=}C(F)-\overset{+}{C}HOR\right]} \xrightarrow{ROH} \rightarrow$$

$$\rightarrow \underset{\text{(XXXVIII), 80\%}}{CH_2{=}CFCH(OR)_2} \xrightarrow{H^+} \underset{\text{(XXXIX), 83\%}}{CH_2{=}CFCHO}$$

Reaction of chlorofluorocarbene with butyl vinyl ether results in the formation of 1-fluoro-1-chloro-2-butoxycyclopropane (XXXVI). Thermal scission of the ring occurs via the formation of allyl cation (XXXVII) to give the dialkyl acetal (XXXVIII), decomposition of which yields fluoroacrolein (XXXIX). This method was used to obtain 15 kg of α-fluoroacrolein.

Fluoroacrolein was subsequently used to prepare phenyl α-fluoroacrylate.[59] The synthesis was conducted in the following manner:

$$CH_2{=}CFCOH \xrightarrow[h\nu]{Br_2} \underset{\text{(XXXIV)}}{CH_2BrCFBrCOBr} \rightarrow \underset{\text{(XL)}}{}$$

$$\xrightarrow[C_5H_5N,CCl_4]{PhOH} \underset{\text{(XLI), 78\%}}{CH_2BrCBrFCO_2Ph} \xrightarrow[(iso\text{-}Pr)_2O]{Zn} \underset{\text{(VIb), 79\%}}{CH_2{=}CFCO_2Ph.}$$

Fluoroacrolein (XXXIX) was mixed with liquid bromine at −5 °C, and the mixture was then refluxed while exposed to UV radiation from a mercury lamp. The resulting acid bromide (XL) was converted in the usual manner to phenyl 2,3-dibromo-2-fluoropropionate (XLI). Dehalogenation of ester (XLI) gives phenyl α-fluoroacrylate (VIb) (61% yield based on α-fluoroacrolein).

A further method for preparing phenyl α-fluoroacrylate (XLII), starting from 1-ethoxy-1-phenoxyethylene, has been developed.[60–64]

$$\underset{\text{(XLII)}}{CH_2{=}C(OEt)(OPh)} \xrightarrow[R_4NCl,CH_2Cl_2]{CHFCl_2,KOH,0^\circ C} \underset{\text{(XLIII), 76\%}}{CH_2-\overset{F}{\overset{|}{C}}(Cl)-C(OEt)(OPh)} \xrightarrow[160\ mm\ Hg]{200^\circ C} \underset{\text{(VIb), 77\%}}{CH_2{=}CFCO_2Ph.}$$

Table 1. Physical properties of α-fluoroacrylic acid derivatives $CH_2=CFR$.

R	Method of synthesis	Initial compound	Yield, % based on initial compound	b.p. °C (mm Hg)	n_D^{20}	d_4^{20}	Refs.
COOH	II.1	CH_2FCO_2Et[a]	21—26	—	—	—	[11]
	II.2	$CH_2=CHCH_2OH$[b]	13	—	—	—	[35]
	II.4	$CH_2=CHCO_2Me$	5	—	—	—	[46, 49]
C(O)F	II.4	$OCH_2CF_2CF_2$	65—67	—	—	—	[55, 56]
	II.3	$CH_2BrCHBrCH_2Cl$	35—47	28	1.3428	1.2114	[43]
	II.4	$CHF_2CF_2CH_2OH$	45	—	—	—	[65]
C(O)Cl	II.1	CH_2FCO_2Et	10—12	60	—	—	[11]
	II.1	»	45	65—67	—	—	[26, 27]
	II.3	$CH_2=CHCO_2Me$	24	64	1.4070	1.2786	[37]
	II.3	$CH_2BrCHBrCH_2Cl$	25—31	60—64	—	1.2980	[43]
$CONH_2$	II.1	CH_2FCO_2Et[c]	13—24	—	—	—	[10, 11, 19]
	II.1	»[d]	55	—	—	—	[9]
$CON(CH_3)_2$	II.1	»	20	55 (12)	—	—	[11]
CN	II.1	»	17	34—36	—	—	[11, 19]
	II.1	»	10	36	—	—	[9]
C(O)H	II.4	$CH_2=CHOBu$	52.5	71—72	—	—	[58]
	II.4	$CH_2=CHOEt$	38	80—85	—	—	[64]
CO_2Me	II.3	$CH_2=CHCO_2Me$	16	90.5—91.7	1.3880	1.1092	[37]
	II.3	$CH_2BrCBrClCO_2Me$	68	91	1.3915	1.1140	[43]
	II.1	CH_2FCO_2Me	40	95	—	—	[11, 16]
	II.4	$OCH_2CF_2CF_2$ | $CH_2BrCHBrCH_2Cl$	54—56	45 (130)	—	—	[55]
	II.3		26—40	41 (110)	1.390	1.1140	[97]
CO_2CO_3	II.4	$OCH_2CF_2CF_2$ | CH_2FCO_2Et	35—40 (66)	—	—	—	[53]
CO_2Et	II.1		25—41	107—109	1.3940	—	[3, 6, 7, 10, 11]
	II.1	»	64	52 (80)	—	—	[9]
	II.4	$CH_2BrCBrFCO_2Et$	70	110 (728)	1.3940	—	[47, 48]
	II.3	$CH_2BrCHBrCH_2Cl$	26—40	109 (750)	1.3925	1.0555	[43]
$CO_2CH_2CF_3$	II.3	»	—	41 (100)	1.345	1.348	[97]
	II.4	$OCH_2CF_2CF_2$	48	28 (30)	—	—	[55]
$CO_2CH_2CCl_3$	II.4	$OCH_2CF_2CF_2$	46	46 (2)	—	—	[55]
$CO_2CH_2(CF_2)_2H$	II.4	»	49	42 (12)	—	—	[55]
	II.3	$CH_2BrCHBrCH_2Cl$	38	62 (30)	1.360	1.418	[97]
$CO_2CH(CF_3)_2$	II.1	$CHF(CO_2Et)_2$	32	46.8 (160)	1.3145	1.453	[26, 27]
$CO_2CO(CF_3)_2$	II.1	»	34	47 (150)	—	—	[25]
$CO_2CF(CF_3)_2$	II.1	»	32	40 (123)	—	—	[25, 26]
$CO_2CH_2CF(CF_3)_2$	II.3	$CH_2BrCHBrCH_2Cl$	26—40	122 (760)	1.331	1.507	[97]
$CO_2C(CH_3)_2CF_2CF_2H$	II.3	»	—	63 (30)	1.377	1.514	[97]
$CO_2CH_2(CF_2)_4H$	II.4	$OCH_2CF_2CF_2$ | $CH_2BrCHBrCH_2Cl$	47	38—42 (4)	—	—	[55]
	II.3		26—40	70 (21)	1.347	1.548	[43, 97]
$CO_2CH_2(CF_2)_6H$	II.3	»		97—101 (17)	1.342	1.632	[97]
$CO_2(CH_2)_3(CF_2)_8H$	II.4	$OCH_2CF_2CF_2$ | »	47	86 (4)	—	—	[55]
$CO_2CH_2(CH_2)_4CH_2$	II.4	»	37	53 (4)	—	—	[55]
$CO_2CH_2C(Me)_2CH_2CH(Me)CH_2$ | CO_2Ph	II.4	»	52	48 (2)	—	—	[55]
	II.4	»	42	43—46 (2)	—	—	[55]
	II.4	$CH_2=CHOEt$	40	52—54 (0.5)	—	—	[60, 63, 64]
	II.4	$CH_2=CFC(O)H$	61.5	52—54 (0.5)	—	—	[58]
	II.1	CH_2FCO_2Et	60[g]	40 (0.2)	—	—	[20, 21]
	II.3	$CH_2BrCHBrCH_2Cl$	26—40	78 (5)	1.5030	1.1756	[43]
$CO_2C_6F_5$	II.3	»	—	59 (3)	1.426	1.549	[97]
	II.1	$CHF(CO_2Me)_2$	38	41—42 (1.5)	—	—	[24][i]
$CO_2C_6Cl_5$	II.1	»	42	—	—	—	[24b]
$CO_2C(CF_3)_2C_6H_5$	II.1	»	26	66 (4)	—	—	[25b]
CO_2-*p*-$C_6H_4P(O)(Ph)_2$	II.3	$CH_2=CFCOCl$[f]	—	—	—	—	[44, 45][j]
$CO_2CH_2CH_2OH$	II.2	$CH_2=CHCH_2OH$	21	81—83 (3)	1.4365	1.2318	[9b]
$CO_2CH_2CH(OH)CH_3$	II.2	»	21	66—68 (3)	1.4328	1.1688	[9b]
$CO_2CH_2CH(OH)CH_2Cl$	II.2	»	21	90—93 (4)	1.4631	1.3200	[9b]

Note. [a] m.p. = 50—51 °C; [b] m.p. = 51.5—52 °C; [c] m.p. = 115—116 °C; [d] m.p. = 116 °C; [e] m.p. = 93—95 °C; [f] m.p. = 114—144.5 °C; [g] yield of crude product is given. [h] Heumüller et al.[24] also report the m.ps. and b.p. of other esters with the formula $CH_2=CFCO_2R$, where R = *o*-, *m*-, and *p*-substituted phenyl groups. [i] In one patent[25] b.ps. are given for compounds with the general formula $CH_2=CFCO_2C(CF_3)_2R$, where R = *m*- and *p*-substituted phenyl groups, furyl and thienyl groups. [j] Lapin et al.[44,45] also give the m.ps. of α-fluoroacrylates of the *ortho*- and *meta*-derivatives of hydroxyphenyldiphenylphosphine oxide.

The unsaturated acetal (XLII), on reaction with chlorofluorocarbene, forms 1-fluoro-2-phenoxy-1-chloro-2-ethoxycyclopropane (XLIII). Thermolysis of cyclopropane (XLIII) under vacuum gives phenyl α-fluoroacrylate (VIb) in good yield.

Recently an original three-stage method for the synthesis of α-fluoroacrylyl fluoride (XXXI) from tetrafluoro- and trifluoro-chloro-propanol was proposed.[65]

$$\underset{\text{(XLIV)}}{HCFXCF_2CH_2OH} \xrightarrow{2RLi} \underset{\text{(XLV)}}{CFX{=}CFCH_2OH} \xrightarrow{H^+} \underset{\text{(XXXI)}}{CH_2{=}CFCOF}.$$

X=Cl, F; R=Me, Bu.

At the first stage alcohol (XLIV) is dehydrofluorinated by alkyl lithium and the resulting allyl alcohol (XLV) is converted to acid fluoride (XXXI) by heating with concentrated sulphuric acid.

III. Physical and chemical properties of α-fluoroacrylic acid derivatives

1. Physical properties

During the last few years a large number of α-fluoroacrylic acid derivatives—halides, amides, nitriles, and alkyl, fluoroalkyl, and aryl esters—have been obtained. The syntheses of most of these compounds have been carried out mainly in order to obtain from them homo- and co-polymers with valuable properties. Therefore, most of the available data on the properties of α-fluoroacrylic acid derivatives appears in patent literature and only a few scientific publications have been devoted to a study of the chemical properties of alkyl and fluoroalkyl α-fluoroacrylates. All of the published data on the physical properties of α-fluoroacrylic acid derivatives are given in Table 1, with the methods of preparation, yields of these monomers, and the literature sources being indicated.

2. Heterolytic reactions of α-fluoroacrylates

Information about the reactivity of α-fluoroacrylate esters towards nucleophilic and electrophilic reagents is extremely limited.[41,47,66,67] Nucleophilic reagents such as alcohols, mercaptans, malonate and acetaminomalonate esters in the presence of alkali metal alkoxides readily add to ethyl α-fluoroacrylate. The direction of addition is such that the nucleophile adds to terminal electron-deficient methylene group of the C=C double bond:[66]

$$CH_2{=}CFCO_2Et \left\{ \begin{array}{ll} \xrightarrow{EtOH,EtONa} & EtOCH_2CHFCO_2Et \ (66\%) \\ \xrightarrow{BuSH,BuOK} & BuSCH_2CHFCO_2Et \ (90\%) \\ \xrightarrow{CH_2(CO_2Et)_2,EtONa} & (EtOCO)_2CHCH_2CHFCO_2Et \ (41\%) \end{array} \right.$$

This is completely analogous to the direction of addition of nucleophiles to unsubstituted acrylates and α-chloro- and α-bromo-acrylates.[68]

Ammonia and amines do not add to the C=C bond of ethyl α-fluoroacrylate but give α-fluoroacrylamides,[66] whereas ammonia readily adds to alkyl α-bromoacrylates to form 2-bromo-3-amino-propionate esters.[69]

Electrophilic reagents such as nitronium fluoride,[66] mercuric nitrate,[66] and bromine monofluoride[41] can also add to the carbon–carbon double bonds of alkyl α-fluoroacrylates. In contrast to unsubstituted acrylates,[70] α-fluoroacrylates add the positively polarised residues of electrophilic reagents to the β-carbon atom:

$$CH_2{=}CFCO_2R \left\{ \begin{array}{ll} \xrightarrow{HNO_3,HF} & O_2NCH_2CF_2CO_2R \ (53\%) \\ \xrightarrow[EtOH]{Hg(NO_3)_2} & O_2NOHgCH_2CFCO_2R \ (48\%) \\ & \quad | \\ & \quad OEt \\ \xrightarrow{1/3(BrF_3+Br_2)} & CH_2BrCF_2CO_2R \ (39\%) \end{array} \right.$$

Electrophilic reagents add to methyl α-chloroacrylate in a similar manner.[41,66] However, the direction of addition of such typical electrophiles as methyl- and phenyl-sulphenyl chlorides to alkyl α-fluoroacrylates is different—the alkylthio and arylthio residues mainly add to the α-carbon atom.[67]

$$CH_2{=}CFCO_2Et \left\{ \begin{array}{ll} \xrightarrow{MeSCl} & CH_2ClCF(SMe)CO_2Et \ (90\%) \\ \xrightarrow{PhSCl} & CH_2ClCF(SPh)CO_2Et \ (68\%) + PhSCH_2CFClCO_2Et \ (22\%) \end{array} \right.$$

Methyl α-fluoroacrylate does not absorb molecular chloride but in the presence of 1–2% tetramethylammonium bromide the reaction with chlorine is very vigorous with evolution of heat, and subsequently on heating α-fluoroacrylate almost the theoretical quantity of Cl_2 is absorbed. It appears that this reaction does not occur by an anionic mechanism as was previously thought[71] but by a free-radical mechanism, since the dimers formed as by-products on chlorination have a structure identical to radical telomers of acrylates:[72]

$$CH_2{=}CFCO_2Me \xrightarrow[Me_4NBr]{Cl_2} CH_2ClCFCO_2Me \xrightarrow{Cl_2} CH_2ClCFClCO_2Me$$

$$CH_2ClCFCO_2Me \xrightarrow{CH_2{=}CFCO_2Me} \begin{array}{l} CH_2ClCFCO_2Me \\ \quad | \\ CH_2CFCO_2Me \end{array} \xrightarrow{Cl_2} \begin{array}{l} CH_2ClCFCO_2Me \\ \quad | \\ CH_2CFClCO_2Me \end{array}$$

Methyl α-chloroacrylate is chlorinated in a similar manner, whereas methyl methacrylate reacts with Cl_2 by an electrophilic mechanism and forms chlorinated dimers through the formation of new C–O rather than C–C bonds.[71]

3. Free-radical reactions of α-fluoroacrylates

a) Radical polymerisation

As was noted in the previous section, the syntheses of α-fluoroacrylic acid derivatives are complex and have multiple stages, so the preparation of significant quantities of the highly pure monomers necessary for studying the kinetics of polymerisation is an extremely laborious process. It is likely that as a result of this, systematic studies on the kinetics of polymerisation of α-fluoroacrylic monomers have not been carried out. Up to the present time only a few studies devoted to this subject have been carried out.[73–79]

Thus, Yamada et al.[73] have studied the radical polymerisation of ethyl α-fluoroacrylate (EFA) in bulk at 30 °C. The fundamental rate constants for chain propagation (K_p) and chain termination (K_t) have been determined, and these are given in Table 2. For comparison, the rate constants for chain propagation and chain termination of other α-substituted acrylates are also shown in Table 2.

The radical copolymerisation of ethyl α-fluoroacrylate with a number of vinyl monomers has been studied and the copolymerisation rate constants determined. From these data it was possible to calculate the fundamental rate constants $K_{2,1}$ and $K_{1,2}$ for ethyl α-fluoroacrylate and the poly(ethyl α-fluoroacrylic) radical. These results and also the corresponding rate constants for methyl acrylate (MA) and ethyl α-chloroacrylate (ECA) are given in Tables 3 and 4.

Table 2. Rate constants of chain propagation (K_p) and termination (K_t) for α-substituted acrylates at 30 °C.[73]

$CH_2=C(X)CO_2R$		$K_p^2/K_t\times10^3$, litre mol^{-1} s^{-1}	K_p, litre mol^{-1} s^{-1}	$K_t\times10^7$, litre mol^{-1} s^{-1}
X	R			
Cl	Et	8.27	1660	48.0
F	Et	2.58	1120	33.3
Me	Me	4.82	450	4.2
H	Me	0.16	720	0.43

Table 3. Reactivity of polymer radicals towards MA, EFA, and ECA at 30 °C.[73]

Monomer	$K_{2,1}$, litre mol^{-1} s^{-1}				
	polystyrene	poly(MMA)	poly(MA)	poly(EFA)	poly(ECA)
MA	141	176	720	6588	516
EFA	240	216	1000	1120	272
ECA	1514	940	7579	5333	1660

Table 4. Reactivity of monomers towards polymer radicals of MA, EFA, and ECA at 30 °C.[73]

Radical	$K_{1,2}$, litre mol^{-1} s^{-1}					
	styrene	MMA	MA	EFA	ECA	AN
poly(MA)	4000	2182	720	1000	7200	1004
poly(EFA)	6222	3394	6588	1120	5333	1120
poly(ECA)	5533	830	520	516	1660	572

[AN = acrylonitrile].

An analysis of these data shows that ethyl α-fluoroacrylate is 3–7 times less reactive than ethyl α-chloroacrylate and has a similar reactivity to that of methyl acrylate. Comparison of the reactivity of the polyradicals of MA, EFA, and ECA also reveals the similarity between the poly(methyl acrylic) and poly(ethyl α-fluoroacrylic) radicals, which are more reactive than the poly(ethyl α-chloroacrylic) radical. These characteristics apparently occur because the fluorine atom stabilises the resulting radical to a much lesser degree than the chlorine atom. This results in ECA having a higher reactivity than EFA and correspondingly the polymer radical of ECA being less reactive than the poly(ethyl α-fluoroacrylic) radical. Gal'perina et al.[76] studied the effect of the solvent on the rate constants of chain propagation and termination in the radical polymerisation of acrylic acid (AA) and α-fluoroacrylic acid (FAA). Water, formamide, and DMSO were used as solvents. The results are given in Table 5.

Table 5. Rate constants of propagation and termination for the polymerisation of AA and FAA in different solvents at 20 °C.[76]

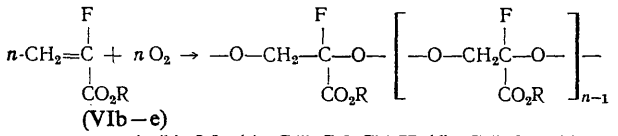
Solvent	FAA		AA	
	K_p, litre mol^{-1} s^{-1}	$K_t\times10^{-8}$, litre mol^{-1} s^{-1}	K_p, litre mol^{-1} s^{-1}	$K_t\times10^{-8}$, litre mol^{-1} s^{-1}
Water	2600±200	0.87±0.07	27 200±200	1.8±0.15
Formamide	2200±200	0.74±0.07	4 200±20	1.0±0.2
DMSO	850±50	0.49±0.01	500±50	0.2±0.01

As can be seen from the results presented, the rate constants of propagation decrease on going from water to DMSO, which is due to the fact that DMSO has the greatest capacity to form complexes with a polymer radical. The marked difference between the values of K_p in the polymerisation of FAA and AA in water is apparently governed by the reactivity of the polymer radicals. The presence of a fluorine atom at the α-position causes a reduction in density of the unpaired electron in a polymer radical, which results in a decrease in reactivity of the polymer radicals of FAA. The difference between the values of K_p in polymerisation between a polymer radical and solvent is considerably less. In the polymerisation of FAA the probability of forming such a complex is much less than in the polymerisation of AA, which leads to a greater decrease in reactivity of AA.

The kinetics of the polymerisation of 2,2,3,3-tetrafluoropropyl α-fluoroacrylate (FN-1) and its methacrylate analogue were recently studied.[79] It was shown that under the same conditions 2,2,3,3-tetrafluoropropyl α-fluoroacrylate polymerises at a much higher rate than 2,2,3,3-tetrapropyl methacrylate (MN-1) and its polymerisation is accompanied by a greater reaction enthalpy. Thus, K_p/K_t is 1.15 (litre mol^{-1} s^{-1})$^{0.5}$ for FN-1 and 0.22 (litre mol^{-1} s^{-1})$^{0.5}$ for MN-1. The polymerisation enthalpy is equal to −73 kJ mol^{-1} for FN-1 and is −57 kJ mol^{-1} for MN-1.

b) Autooxidation by atmospheric oxygen

α-Fluoroacrylates, in the same way as other vinyl monomers,[80–82] are oxidised by atmospheric oxygen to give peroxides that consist of alternating copolymers of monomers and oxygen.[83,84]



(VIb–e)

R = Ph (b), Me (c), $CH_2CF_2CF_2H$ (d), CH_2CF_3 (e); $n = 10 - 20$.

Other conditions being equal, α-fluoroacrylate esters absorb oxygen much more rapidly (by a factor of 100 or more) than their acrylate and methacrylate analogues (Table 6). It would appear that there are no parallels amongst acrylic or other vinyl monomers with respect to the rate of oxidation of α-fluoroacrylates by air.

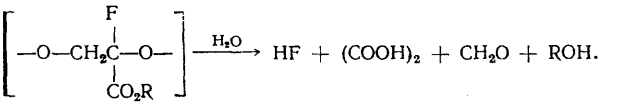
Table 6. Absolute and relative rates of oxidation (W) of monomers $CH_2=CXCO_2R$ by atmospheric oxygen at 50 °C (concentration of initiator AIBN = 8.6×10^{-2} mol litre^{-1}).[83]

Monomer		$W \times 10^5$, mol litre^{-1} s^{-1}	W_{rel}
X	R		
H	$CH_2(CF_2)_2H$	0.05	1
Me	$CH_2(CF_2)_2H$	0.17	3.4
F	Me	10.7	210
F	$CH_2(CF_2)_2H$	11.9	240
F	CH_2CF_3	43.0	360

In two studies[4,5] the greatest attention was given to phenyl and tetrafluoropropyl esters of α-fluoroacrylic acid and to the properties of their polyperoxides. The rate of oxidation of tetrafluoropropyl α-fluoroacrylate initiated by azobis(isobutyronitrile) (AIBN) on temperature was studied and the ratio of the rate constants of chain propagation (K_p) and chain termination (K_t) was calculated as $(K_p/K_t) = 7.4 \times 10^3 e^{-7034/RT}$.

As is evident from this equation, the oxidation of tetrafluoropropyl α-fluoroacrylate over the temperature range 40–60 °C has an energy of activation (7 kcal mol^{-1}) that is much lower than that of methyl methacrylate (10.5 kcal mol^{-1}).[80]

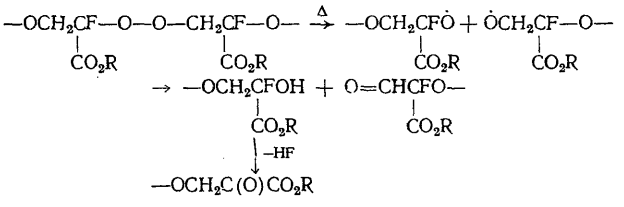
The peroxides of fluoroalkyl and aryl α-fluoroacrylates readily decompose when treated with nucleophilic reagents such as alkalis, alcohols, and water. The hydrolysis products of the peroxides of tetrafluoropropyl and phenyl α-fluoroacrylate provide confirmation that their structure consists of alternating copolymers with oxygen:



R = Ph (VIb), $CH_2CF_2CF_2H$ (VId)

The hydrolytic decomposition of the peroxides of these monomers in dioxan and tetrahydrofuran occurs at temperatures considerably below the temperature range of their thermal decomposition.[83,84]

The thermolysis of peroxides of tetrafluoropropyl and phenyl α-fluoroacrylates takes place with the evolution of gaseous HF (0.5 to 0.8 moles per mole equivalent of peroxide). Panteleeva et al.[83,84] attribute the evolution of HF to the disproportionation of primary radicals in the solvent cage, as a result of which unstable fluorohydroxy compounds are formed:



The kinetics of the thermal decomposition of peroxides of phenyl and fluoroalkyl α-fluoroacrylates in hydrophobic solvents have been studied. Kinetic data on the thermolysis of these peroxides correlated against similar data on their acrylate, methacrylate, and α-chloroacrylate analogues and benzoyl peroxide are given in Table 7.[83–85] It is clear from these data that the temperature range of thermolysis of peroxides of α-haloacrylates is considerably lower than for their acrylate and methacrylate analogues. The thermolysis characteristics of α-fluoroacrylate peroxides are similar to those of the widely used medium-temperature radical initiator—benzoyl peroxide. It is probable that the high rate of oxidation of α-fluoroacrylates at normal temperatures is due to the relatively low temperature range of thermal decomposition of their own peroxides, as a result of which these peroxides effectively initiate the radical chain autooxidation of the monomers.

Table 7. Kinetic data on the thermal decomposition of peroxides $-(-OCH_2CXO-)-$ in solution* (initial concentration of peroxides = $4-20 \times 10^{-2}$ equivalents litre^{-1}.

No.	X	R	T, °C	$K \times 10^5$, s^{-1}	E, kcal mol^{-1}	Refs.
1	H	Ph	120.0	8.3	28.0	[85]
2	Me	Ph	100.0	6.8	32.4	[85]
3	Cl	Ph	75.3	7.9	25.6	[85]
4	F	Ph	75.0	2.9	27.5	[84]
5	F	$CH_2(CF_2)_2H$	73.0	5.6	31.5	[83]
6	F	CH_2CF_3	72.5	8.2	29.9	[83]
7	benzoyl peroxide		79.9	3.3	32.7	[86]

*Peroxides 1–4 and 7 in chlorobenzene, peroxides 5 and 6 in $MeCO_2CH_2CF_2CF_2H$.

Thus, the low thermal and hydrolytic stability of α-fluoroacrylate polyperoxides assists on the one hand the rapid formation of polyperoxides in monomers and on the other hand their rapid

decomposition, which accompanies the formation of decomposition products. Taking into account the high rate of radical polymerisation of these monomers, it may be assumed that stabilisation of their properties will present a more complex problem than the stabilisation of acrylates and methacrylates.

IV. Properties and use of polymers

Fluorinated polymers have played a very large role in present-day technology because of their stability when used under extreme conditions.[87–89]

Studies of recent years have shown that α-fluoroacrylate polymers have many working characteristics that are significantly superior to those of their methacrylate analogues. The introduction of fluorine into the α-position relative to the acrylate ester group resulted in an improvement in the properties of block organic glass on the basis of its heat resistance and impact resistance.[21,90,91] Amongst polymers of this class poly(phenyl α-fluoroacrylate) has the best properties, so it could be recommended as a construction material for the glazing of cockpits in high-speed aircraft.[21,59,91]

In Table 8 the effect of introducing fluorine into the α-position on the heat-resistance of block acrylic homopolymers is demonstrated.

Table 8. Softening point of block homopolymers of α-substituted acrylate esters.

Monomer	T_s, °C	Refs.	Monomer	T_s, °C	Refs.
$CH_2=CHCO_2Me$	3	[73]	$CH_2=CClCO_2Me$	145	[73]
$CH_2=CHCO_2Et$	−22	[73]	$CH_2=CClCO_2Et$	94	[73]
$CH_2=CHCO_2Ph$	55	[92]	$CH_2=CFCO_2Me$	142	[73]
$CH_2=C(CH_3)CO_2Me$	120	[73]	$CH_2=CFCO_2Et$	94	[73]
$CH_2=C(CH_3)CO_2Et$	65	[92]	$CH_2=CFCO_2Ph$	180	[91]
$CH_2=C(CH_3)CO_2Ph$	110	[92]			

These data indicate that the heat resistance of polyacrylic polymers is significantly affected not only by the substituent at the α-position relative to the ester group but also by the structure of the substituent in the ester part of the molecule. Usually polar and bulky substituents increase the softening point of the polymers.[92] α-Halogenated polyacrylate esters have the greatest heat resistance, with α-chloro- and α-fluoro-acrylic polymers having the same value of T_s. However, more fundamental studies on these polymers showed that α-fluoroacrylates are very much superior to α-chloroacrylates in terms of their thermal stability (from the loss of weight at elevated temperatures).[73] Thermogravimetric analysis of poly(methyl fluoroacrylate) [poly(MFA)], poly(ethyl fluoroacrylate) [poly(EFA)], and poly(ethyl chloroacrylate) [poly(ECA)] showed that polyacrylic polymers undergo thermal depolymerisation over a narrow temperature range with a maximum rate of decomposition at 400 °C for poly(MFA) and 370° for poly(EFA). The decomposition of poly(ECA) starts at as low a temperture as 180 °C, it is a more complex process and involves not only depolymerisation but also dehydrochorination.[73] Research workers attribute the high thermal stability of α-fluoroacrylates to the greater stereoregularity of poly(α-fluoroacrylate) radicals, namely, to their higher content of isotactic diads.[73,93,94]

The high chemical stability of polymethyl and polyphenyl α-fluoroacrylates is also likely to be related to structural features.

The thermal decomposition of certain poly(α-fluoroacrylates) has been studied.[95,96] The rates of weight loss of polymers (w) when the degree of decomposition is 10% and the energy of activation of thermal decomposition (E) of poly(methyl α-fluoroacrylate) (PMFA) and poly(1,1,5-trihydrooctafluoroamyl α-fluoroacrylate) (PFAFA) correlated with their acrylate analogues—poly(methyl methacrylate) (PMMA) and poly(1,1,5-trihydrooctafluoroamyl acrylate) (PFAA)—are given in Table 9.

Table 9. Kinetic data on thermal decomposition of polymers.[95]

Polymer	$w \times 10^2$, % s^{-1} at a temperature of (°C):						E, kcal mol^{-1}
	300	310	320	330	340	350	
PMA	0.11	0.15	0.31	0.83	1.52	3.18	45.4
PMFA	0.07	0.13	0.17	0.34	0.64	1.29	50.2
PFAA	0.05	0.12	0.17	0.40	0.59	1.05	28.7
PFAFA	0.06	0.12	0.26	0.46	0.83	1.46	44.2

The data on the thermal decomposition of poly(α-fluoroacrylates) show that the latter have comparable thermal stability to that of polyacrylates that are unsubstituted at the α-position. Gorelov et al.[95,96] attribute the substantial difference in the values of the energy of activation to the different types of reactions that occur during thermal decomposition.

Further studies on poly(α-fluoroacrylates) revealed another promising area of their application—as optical materials in the priority area of the present-day technology of information communication and transmission, namely, fibre optics.[97,99–107] The outstanding optical properties of these polymers combined with their improved heat resistance, flexibility, and moisture resistance give them a considerable advantage over fluorine-containing methacrylates which have been widely studied and used in fibre optics. At the present time many new α-fluoroacrylic monomers and polymers have been synthesised and patented; they have a wide range of refractive index (1.36–1.50), so they could be used as materials for a light-guiding centre and light-reflective membrane.[99–107]

Boguslavskaya et al.[97] carried out a comparative study of the optical and physicomechanical properties of fluoroalkyl α-fluoroacrylate and methacrylate polymers. The molecular weight of block polymers are usually in the range 1 000 000–5 000 000. The properties of the polymers were correlated according to the following parameters: the transmission factor (K_{tr}), refractive index (n_D), softening point (T_s), impact strength (a_n), tensile strength at break (σ_b), specific elongation at break (ε_b), and also the thermal stability relative to visible degradation (T_{stab}). In this case the thermal stability denotes the maximum temperature at which heating a sample for 2 h does not produce any defects (bubbles, cracking, etc.). The results are given in Table 10.

Table 10. Properties of block polymers.

Monomers	K_{tr}, %	n_D^{20}	T_s, °C	a_n, kJ m^{-2}	σ_b, MPa	ε_b, %	T_{stab}	Refs.
$CH_2=CFCO_2R$								
R=Me	91	1.459	140	22	96	4.6	240	[97]
$CH_2CF_2CF_2H$	91	1.398	95	21	54	66	230	[97,99]
$CH_2(CF_2CF_2)_2H$	90	1.379	77	—	18	24	—	[97]
$CH_2CF_2CF_3$	—	1.370	105	—	—	—	—	[99]
CH_2CF_3	91	1.385	123	17	63	12.5	220	[97,99]
$C(CH_3)_2CF_2CF_2H$	90	1.400	133	—	—	—	—	[97,99]
$C(CF_2)_2CF_2CF_2CF_3$	90	1.330	60	—	—	—	—	—
$CH_2CF(CF_3)_2$	90	1.360	108	—	—	—	200	[97,99]
C_6F_5	86	1.457	174	4	56	3.1	210	[97,102]
$CH_2=C(CH_3)CO_2R$								
R=Me	90	1.491	113	10	77	3.3	180	[97]
$CH_2CF_2CF_2H$	91	1.422	71	6	47	2.7	170	[97]
$CH_2(CF_2CF_2)_2H$	91	1.400	50	—	—	—	—	[97]
$CH_2CF_2CF_3$	—	1.395	72	—	—	—	—	[108]
CH_2CF_3	91	1.416	76	7	48	2.0	180	[97,108]
$C(CF_3)CF_2CF_2CF_3$	90	1.346	62	—	—	—	—	[97]
C_6F_5	—	1.487	115	—	—	—	—	[102]

It can be seen from Table 10 that block poly(fluoroalkyl α-fluoroacrylates) with relatively short fluoroalkyl residues (1–3 carbon atoms) have considerably higher values of the softening point (more than 20 °C) and thermal stability (40–60 °C) than their methacrylate analogues. Poly(α-fluoroacrylates) are superior to their methacrylate analogues in terms of impact strength, tensile strength, and elasticity, and they have a higher level of deformation-strength properties at high temperatures.[97,108] Moreover, α-fluoroacrylic polymers are more stable towards various ageing factors (effect of heat and moisture) than the corresponding methacrylates.[97,99] In addition to fibre optics, fluoroalkyl α-fluoroacrylates can be used as materials for optical storage systems such as optical disks.[102,109]

Highly fluorinated compounds usually dissolve oxygen effectively. This property of poly(fluoroalkyl α-fluoroarylates) has been utilised when they were patented as effective gas-separation membranes[110–112] that are superior to their methacrylate analogues in terms of oxygen permeability and mechanical strength.

$$-(-CH_2-\underset{\displaystyle CO_2(CH_2)_m CFX(OCH_2CFX)_n OPr}{\underset{|}{CF}}-)-$$

X=F, fluoroalkyl (C_{1-3}); $m=1-3$; $n=0-5$.

Fluoroacrylic polymers which contain OH groups in the ester part of the molecule have been suggested as materials for contact lenses.[113,114]

$$-(-CH_2)-\underset{\displaystyle CO_2(CH_2)_m R}{\underset{|}{CF}}-)-$$

R – fluoroalkyl with OH group; $m=1-5$.

α-Fluoroacrylic polymers with improved mechanical strength have been patented as dental prosthetic materials.[115] Poly(methyl α-fluoroacrylate) can undergo decomposition when exposed to certain forms of radiation (UV, X-rays) and can be used in semiconductor technology for the manufacture of photoresistors.[74,87] Fluoroacrylic polymers can also be used in other areas of industry such as in paint production.[12,13,15]

The unique properties of polymeric α-fluoroacrylates, as is evident from the previous section of this review, when they are widely applied can give rise to substantial progress in many areas of technology and medicine.

A restriction on the application of these materials arises from the fact that so far no methods exist for preparing monomers of this class that are suitable for the development of an industrial process. Not one of the methods examined in Section II satisfies the current strict requirements for simplicity of design, safety, and ecological purity. Whilst amongst the group of traditional acrylic monomers, acrylic and methacrylic acids are the main members of the series and constitute starting materials for the synthesis of the remaining monomers, it is unlikely that α-fluoroacrylic acid could be used as a starting material for α-fluoroacrylates. In contrast to liquid acrylic and methacrylic acids, α-fluoroacrylic acid is a solid (m.p. 51 °C), so that it is extremely difficult to stabilise it against uncontrolled polymerisation. Consequently, the methods of preparation of α-fluoroacrylates are fundamentally different from those for acrylates and methacrylates, and even when produced on a small scale α-fluoroacrylates can have a considerable impact on the development of novel systems and compounds providing current technological progress. Therefore, future research into improved methods of

obtaining α-fluoroacrylic monomers, polymers, and composite materials is a promising area of organofluorine synthesis.

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