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Reactions of acrylic acid with fluoroalkanoyl peroxides – the formation of acrylic acid oligomers containing two fluoroalkylated end-groups

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Abstract

Fluoroalkylated acrylic acid oligomers were obtained by oligomerizations of acrylic acid with fluoroalkanoyl peroxides. Elemental analyses for fluorine showed that these oligomers contain two fluoroalkylated end-groups in one oligomeric molecule. Perfluoro-oxa-alkyl radicals produced by the decomposition of the corresponding peroxides have been demonstrated as being more stable than perfluoroalkyl radicals, and their higher stabilities explain the formation of higher molecular weight in the perfluoro-oxa-alkylated acrylic acid oligomers.

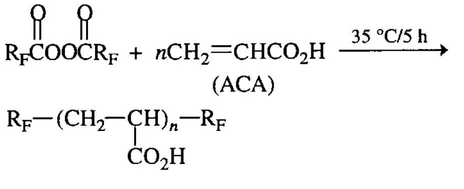
Introduction

We have demonstrated recently that fluoroalkanoyl peroxides [$(R_FCO_2)_2$] possessing perfluoroalkyl [$R_F = CF_3(CF_2)_n$, $n = 0, 1, 2, 5, 6$] and perfluoro-oxa-alkyl {$R_F = C_3F_7O[CF(CF_3)CF_2O]_mCF(CF_3)$, $m = 0, 1, 2$} groups are effective tools for the introduction of the corresponding fluoroalkyl groups into various substrates [1]. In particular, fluoroalkanoyl peroxides have been shown to be useful precursors for the generation of fluoroalkyl radicals. Hence, a radical process using fluoroalkanoyl peroxides provides a novel synthetic strategy for fluoroalkylations with carbon–carbon bond formation.

In the reactions of acrylic acid with fluoroalkanoyl peroxides, we reported that fluoroalkylated acrylic acid oligomers with carbon–carbon bond formation are obtained in moderate to excellent yield under mild conditions via radical processes [2]. Fluoroalkylated acrylic acid oligomers were also found to show surface properties typical of amphipathic compounds [2]. However, the novel oligomerization mechanisms for such reactions have not yet been clarified. In this paper, we wish to report on the mechanisms for the oligomerization of acrylic acid with fluoroalkanoyl peroxides and to discuss, in particular, the formation of fluoroalkylated acrylic acid oligomers using both the MNDO PM-3 molecular orbital (MO) method and elemental analysis.

Results and discussion

Previously, we reported that fluoroalkanoyl peroxides react with the acrylic acid monomer (ACA) to afford the corresponding fluoroalkylated oligomers with carbon–carbon bond formation as shown in Scheme 1 [2].



$$R_FC(=O)OOC(=O)R_F + nCH_2{=}CHCO_2H \xrightarrow{35\ ^\circ C/5\ h} R_F{-}(CH_2{-}\underset{\displaystyle CO_2H}{CH})_n{-}R_F \qquad (1)$$

(ACA)

($R_F = C_3F_7$, C_6F_{13}, $C_3F_7O[CF(CF_3)CF_2O]_mCF(CF_3)$; $m = 0, 1, 2$)

Scheme 1.

Reactions of fluoroalkanoyl peroxides with acrylic acid were considered to proceed by the usual radical addition of $R_F^\bullet$ to acrylic acid. Hence, some of the fluoroalkylated acrylic acid oligomers were suggested as containing only one fluoroalkylated end-group per molecule. We tried to synthesize acrylic acid oligomers containing various fluoroalkyl groups (perfluoro-oxa-

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alkyl and perfluoroalkyl) in the same manner and the results are listed in Table 1.

As listed in Table 1, the molecular weights of fluoroalkylated acrylic acid oligomers are markedly dependent upon the molar ratios of ACA and peroxides, increasing with greater molar ratios of ACA in ACA/peroxides as is usual for radical oligomerizations. In those cases where the concentration of initiator was higher than that of the monomer, a polymer with two initiator fragments was obtained, in general, via primary radical termination of the growing radicals with the radical produced by the initiator [eqn. (2)] or via chain transfer to the initiator [eqn. (3)] as shown in Scheme 2 [3].

$$\mathrm{R{-}R} \longrightarrow$$

$$\mathrm{R\cdot + R\cdot} \xrightarrow{n\mathrm{M}} \begin{cases} \mathrm{R{-}M_{\mathit{n}}\cdot + R\cdot \longrightarrow R{-}M_{\mathit{n}}{-}R} & (2) \\ \mathrm{R{-}M_{\mathit{n}}\cdot \xrightarrow{R-R} R{-}M_{\mathit{n}}{-}R + R\cdot} & (3) \end{cases}$$

Scheme 2.

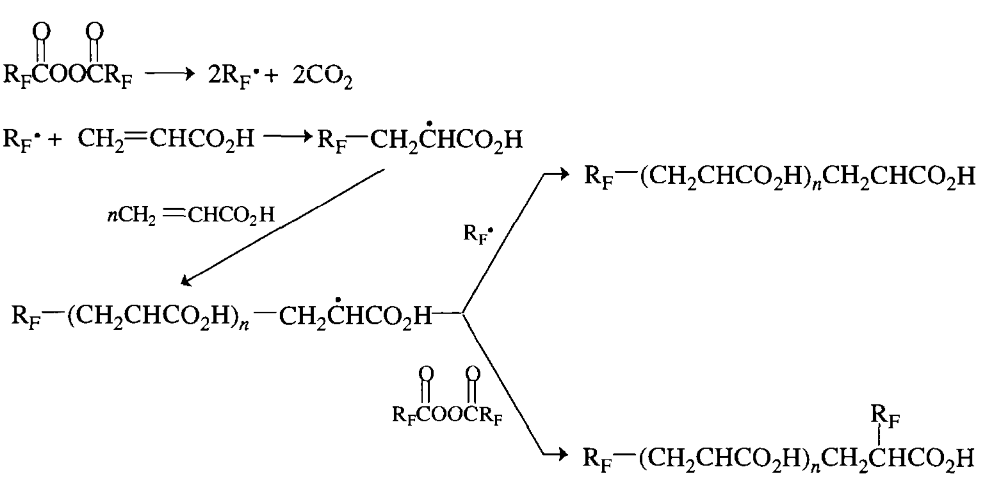
It is suggested that under our oligomeric conditions, in which the concentration of the peroxide was almost the same as that of ACA (molar ratio of ACA/peroxide = 1.0 ~ 5.0), mainly oligomers with two fluoroalkyl groups, i.e. $R_F-(CH_2-CHCO_2H)_n-R_F$, would be obtained via primary radical termination or radical chain transfer to the peroxide. Elemental analyses for fluorine in these oligomers have been performed in order to clarify the structures of the fluoroalkylated acrylic acid oligomers. The results are listed in Table 2.

From Table 2, it is obvious that each oligomer molecule contains two fluoroalkyl groups (two initiator fragments). As shown in Scheme 3, radical chain transfer to the peroxide [eqn. (7)] is suggested as being essential under our oligomeric conditions in which the concentration of the peroxide was almost identical to that of ACA.

TABLE 1. Synthesis of fluoroalkylated acrylic acid oligomers via the reactions of fluoroalkanoyl peroxides $[(R_FCO_2)_2]$ with acrylic acid (ACA)

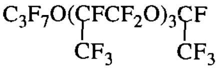
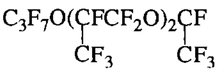
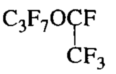
Run No.	R_F in peroxide	ACA (mmol)	Molar ratio (ACA/peroxide)	Yield (%)[a]	$\overline{M}_n(\overline{M}_w/\overline{M}_n)$[b]
1	$C_3F_7O(\underset{CF_3}{C}FCF_2O)_3\underset{CF_3}{C}F$	5.0	0.6	2	8800(1.40)
2	$C_3F_7O(\underset{CF_3}{C}FCF_2O)_3\underset{CF_3}{C}F$	7.7	1.0	4	10660(1.58)
3	$C_3F_7O(\underset{CF_3}{C}FCF_2O)_3\underset{CF_3}{C}F$	18.5	2.4	13	12660(1.70)
4	$C_3F_7O(\underset{CF_3}{C}FCF_2O)_2\underset{CF_3}{C}F$	16.9	1.5	12	10250(1.82)
5	$C_3F_7O(\underset{CF_3}{C}FCF_2O)_2\underset{CF_3}{C}F$[c]	17.0	2.5	29	12800(1.72)
6	$C_3F_7O\underset{CF_3}{C}FCF_2O\underset{CF_3}{C}F$	120	2.4	34	11200(1.54)
7	$C_3F_7O\underset{CF_3}{C}F$	566	2.4	45	12000(1.54)
8	C_6F_{13}	7.7	1.0	9	3460(1.54)
9	C_6F_{13}[c]	6.9	2.4	26	4600(1.43)
10	C_3F_7[c]	204	2.4	39	5100(1.47)

[a] Yields based on starting materials {acrylic acids and the decarboxylated peroxide unit (R_F-R_F)}.
[b] Average molecular weight determined by gel permeation chromatography calibrated with standard polystyrenes.
[c] Cited from ref. 2(a).



Scheme 3.

TABLE 2. Number of fluoroalkyl end-groups in oligomers obtained by the reaction of acrylic acid with fluoroalkanoyl peroxides

R_F in $R_F(CH_2CHCO_2H)_nR_F$	Number of fluoroalkyl end-groups per oligomer molecule[a]	$\bar{M}_n(\bar{M}_w/\bar{M}_n)$
 $C_3F_7O(CF(CF_3)CF_2O)_3CF(CF_3)$	2.4	7400(1.42)
 $C_3F_7O(CF(CF_3)CF_2O)_2CF(CF_3)$	2.2	15500(1.80)
 $C_3F_7OCF(CF_3)$	1.5	15900(1.48)
C_3F_7	1.6	7410(1.65)

[a]Calculated from elemental analysis (fluorine atom) data and M_n values.

The progress of the oligomerization of acrylic acid with perfluoro-2,5-dimethyl-3,6-dioxa-nonanoyl peroxide has also been studied at 40 °C. The results obtained (shown in Table 3) indicate that oligomerization was complete within c. 30 min, to generate a bis(perfluoro-1,4-dimethyl-2,5-dioxa-octyl) acrylic acid oligomer in 48% yield.

The half-life ($\tau_{1/2}=40$ min) of $\{[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CO_2]_2\}$ at 40 °C was estimated by extrapolating the decomposition rates (k_d, s^{-1}) of this peroxide at 10 °C [$k_d=0.82\times10^{-5}$], 15 °C [$k_d=1.42\times10^{-5}$], 20 °C [$k_d=2.70\times10^{-5}$] and 25 °C [$k_d=5.36\times10^{-5}$]. This value for the half-life indicates that the formation of perfluoro-oxa-alkylated oligomer ($R_F-ACA-R_F$) may be attributed not only to primary radical termination [eqn. (6)] but also to radical chain transfer to the peroxide [eqn. (7)] as shown in Scheme 3.

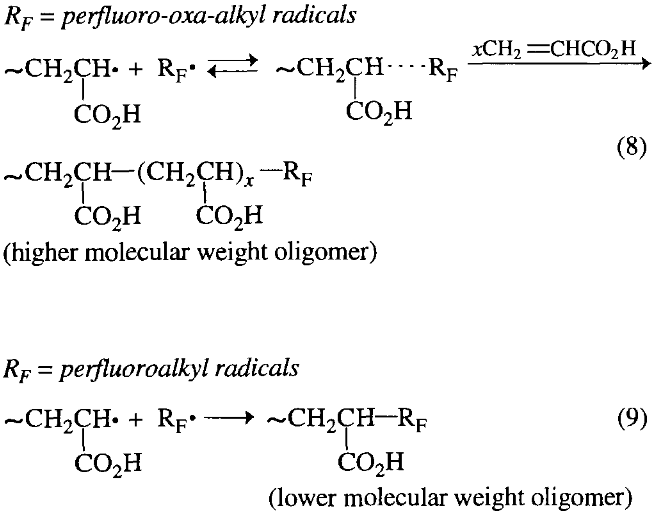
TABLE 3. Molecular weights and yields of perfluoro-oxa-alkylated oligomers in the oligomerization of acrylic acid with $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CO_2]_2$ at 40 °C[a]

Time (min)	Yield of fluoroalkylated oligomer (%)	$\bar{M}_n(\bar{M}_w/\bar{M}_n)$
10	38	10980(1.84)
15	39	11100(1.82)
30	48	9900(1.67)
60	48	11050(1.96)
90	48	12000(1.82)

[a]Molar ratio of ACA/peroxide = 5.0.

Interestingly, there was a general tendency for the molecular weight of $R_F-ACA-R_F$ to increase in perfluoro-oxa-alkylated systems $\{R_F=C_3F_7O[CF(CF_3)CF_2O]_mCF(CF_3)$, $m=0, 1, 2, 3\}$ than in perfluoroalkylated systems [$R_F=CF_3(CF_2)_n$, $n=2, 5$] (see Table 1). However, perfluoro-oxa-alkanoyl peroxides decompose faster than perfluoroalkanoyl peroxides, as follows: $\tau_{1/2}$ (min) for peroxide at 20 °C: $\{C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)CO_2\}_2=261$ [4], $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CO_2]_2=433$ [4], $[C_3F_7OCF(CF_3)CO_2]_2=261$ [4], $(C_7F_{15}CO_2)_2=614$ [4] and $(C_3F_7CO_2)_2=722$ [5]. These results may be attributed to the stabilization of perfluoro-oxa-alkyl radicals. It is well known that the presence of strong donor and acceptor groups attached to a radical centre introduces a synergistic effect on the stabilization of radicals [6]. It should be noted that the interaction between perfluoro-oxa groups $\{C_3F_7O[CF(CF_3)CF_2O]_m$; $m=0, 1, 2, 3\}$ and a trifluoromethyl group (or a fluorine atom) causes additional stabilization of perfluoro-oxa-alkyl groups relative to perfluoroalkyl groups [$CF_3(CF_2)_n$]. Thus, the substitution of both perfluoro-oxa groups and a trifluoromethyl group (or a fluorine atom) brings about a combined action that stabilizes the radical. Recently, Scherer *et al.* discovered the tertiary perfluoroalkyl radical $\{(CF_3)_2CF\dot{C}[CF_2CF_3]CF(CF_3)_2\}$, which is extraordinarily stable even at room temperature [7]. Since perfluoro-oxa-alkyl radicals are secondary, such radicals would be stabilized to a greater extent than perfluoroalkyl (primary) radicals. Furthermore, we have estimated the radical stabilization energies (RSE) of $C_3H_7\cdot$, $C_3F_7\cdot$, $C_3F_7OCF(CF_3)\cdot$ and $(CF_3)_2CF\dot{C}[CF_2CF_3]CF(CF_3)_2$ based on a calculation of the relative difference in 'heat formation' (ΔH) between R_F-H (or R−H) and $R_F\cdot$ (or R·) using a MNDO-PM3 MO method [8]: the results obtained are listed in Table 4.

The RSE values obtained indicate that the substitution of either a C_3F_7O group or two $(CF_3)_2CF$ groups markedly stabilizes the radical compared to $C_3F_7\cdot$ or $C_3H_7\cdot$ radicals. Hence, an increase in the molecular weight of perfluoro-oxa-alkylated oligomers would be dependent upon retardation of the coupling rates in termination reactions as a direct result of their stabilities as shown in Scheme 4.



$$\sim CH_2\underset{CO_2H}{CH}\cdot + R_F\cdot \rightleftarrows \sim CH_2\underset{CO_2H}{CH}\cdots R_F \xrightarrow{xCH_2=CHCO_2H} \sim CH_2\underset{CO_2H}{CH}-(CH_2\underset{CO_2H}{CH})_x-R_F \quad (8)$$

$$\sim CH_2\underset{CO_2H}{CH}\cdot + R_F\cdot \longrightarrow \sim CH_2\underset{CO_2H}{CH}-R_F \quad (9)$$

Scheme 4.

TABLE 4. Radical stabilization energies (RSE) calculated by an MNDO-PM3 MO method

$R_F\cdot$	RSE (kcal mol^{-1})
$C_3H_7\cdot$	44.96
$C_3F_7\cdot$	−12.27
$C_3F_7O\dot{C}F(CF_3)$	−13.19
$(CF_3)_2CF\dot{C}CF(CF_3)_2$ CF_2CF_3	−13.99

In conclusion, we have shown that the reactions of acrylic acid with fluoroalkanoyl peroxides proceed to afford fluoroalkylated acrylic acid oligomers containing two fluoroalkyl end-groups per oligomer molecule via radical processes which resulted from both primary radical termination by the $R_F^{\bullet}$ radical and radical chain transfer from the growing radical to the peroxide. Furthermore, MNDO-PM3 MO calculations indicate that a perfluoro-oxa-alkyl radical is more stable than a perfluoroalkyl radical which would explain the higher molecular weights observed for the perfluoro-oxa-alkylated oligomers.

Experimental

Measurements

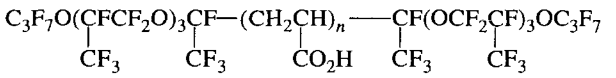
NMR spectra were measured with a JEOL-EX-270 FT-NMR(270 MHz) spectrometer while IR spectra were recorded on a Perkin-Elmer 1600 series FT–IR spectrophotometer. Molecular weights were calculated by using a JASCO 830-RI gel permeation chromatograph filled with Shodex KF-800P, KF-804 and KF-8025 columns (calibration based on polystyrene standards).

Materials

A series of fluoroalkanoyl peroxides $\{(R_FCO_2)_2$; $R_F = C_6F_{13}, C_3F_7, C_3F_7O[CF(CF_3)CF_2O]_mCF(CF_3), m = 3, 2, 1, 0\}$ were prepared from the corresponding acyl halides and hydrogen peroxides in the presence of aqueous sodium hydroxide in 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113) according to our previously reported method [4, 9].

General procedure for the synthesis of fluoroalkylated acrylic acid oligomers

Perfluoro-2,5,8,11-tetramethyl-3,6,9,12-tetraoxa-pentadecanoyl peroxide (7.7 mmol) in Freon-113 solution (210 g) was added to a mixture of acrylic acid (18.5 mmol) and Freon-113 (100 g). The solution was stirred at 35 °C for 5 h under nitrogen when the resulting white powder was reprecipitated from methanol/ethyl acetate to give a bis(perfluoro-1,4,7,10-tetramethyl-2,5,8,11-tetraoxa-tetradecylated) acrylic acid oligomer;

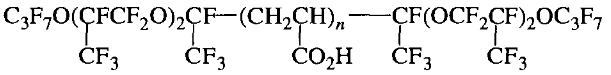


$$C_3F_7O(\underset{CF_3}{C}FCF_2O)_3\underset{CF_3}{C}F-(CH_2\underset{CO_2H}{C}H)_n-\underset{CF_3}{C}F(OCF_2\underset{CF_3}{C}F)_3OC_3F_7$$

(1.74 g). This oligomer exhibited the following spectral characteristics: IR ν (cm^{-1}): 3100 (OH); 1720 (C=O); 1310 (CF_3); 1240 (CF_2). ^{19}F NMR (CD_3OD, ext. CF_3CO_2H) δ: −3.0 to −7.2 (46F); −53.04 (6F); −67.2 (6F) ppm. ^1H NMR (CD_3OD) δ: 1.39–2.06−CH_2−);

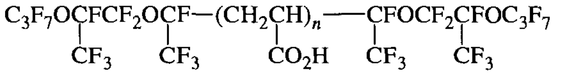
2.25–2.60 (=CH−) ppm. ^{13}C NMR (CD_3OD) δ: 36.10; 42.66; 178.72 ppm.

The following spectral data were obtained for the other products studied:



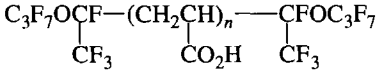
$C_3F_7O(\underset{CF_3}{CF}CF_2O)_2\underset{CF_3}{CF}-(CH_2\underset{CO_2H}{CH})_n-\underset{CF_3}{CF}(OCF_2\underset{CF_3}{CF})_2OC_3F_7$

IR ν (cm^{-1}): 3160 (OH); 1713 (C=O); 1310 (CF_3); 1245 (CF_2). ^{19}F NMR (CD_3OD, ext. CF_3CO_2H) δ: −3.0 to −7.8 (36F); −53.9 (6F); −68.9 (6F) ppm. ^1H NMR (CD_3OD) δ: 1.42–2.10(−CH_2−) ppm. ^{13}C NMR (CD_3OD) δ: 35.97; 42.62; 178.77 ppm.



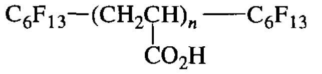
$C_3F_7O\underset{CF_3}{CF}CF_2O\underset{CF_3}{CF}-(CH_2\underset{CO_2H}{CH})_n-\underset{CF_3}{CF}OCF_2\underset{CF_3}{CF}OC_3F_7$

IR ν (cm^{-1}): 3200 (OH); 1720 (C=O); 1335 (CF_3); 1240 (CF_2). ^1H NMR (CD_3OC) δ: 1.35–2.10 (−CH_2−); 2.19–2.80 (=CH−) ppm.



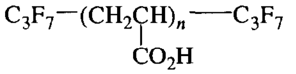
$C_3F_7O\underset{CF_3}{CF}-(CH_2\underset{CO_2H}{CH})_n-\underset{CF_3}{CF}OC_3F_7$

IR ν (cm^{-1}): 3200 (OH); 1720 (C=O); 1330 (CF_3); 1235 (CF_2). ^{19}F NMR (CD_3OD, ext. CF_3CO_2H) δ: −2.1 to −8.9 (16F); −54.3 (6F) ppm. ^1H NMR (CD_3OD) δ: 1.35–2.19 (−CH_2−); 2.21–2.72 (=CH−) ppm. ^{13}C NMR (CD_3OD) δ: 35.40; 42.68; 178.52 ppm.



$C_6F_{13}-(CH_2\underset{CO_2H}{CH})_n-C_6F_{13}$

IR ν (cm^{-1}): 3200 (OH); 1720 (C=O); 1345 (CF_3); 1240 (CF_2). ^{19}F NMR (CD_3OD, ext. CF_3CO_2H) δ: −2.7 (6F); −33.1 (4F); −43.1 (4F); −44.3 (8F); −44.7 (4F) ppm. ^1H NMR (CD_3OD) δ: 1.25–2.19 (−CH_2−); 2.20–3.10 (=CH−) ppm.



$C_3F_7-(CH_2\underset{CO_2H}{CH})_n-C_3F_7$

IR ν (cm^{-1}): 3250 (OH); 1720 (C=O); 1340 (CF_3); 1230 (CF_2). ^{19}F NMR (CD_3OD, ext. CF_3CO_2H) δ: −5.1 (6F); −36.2 (4F); −50.9 (4F) ppm. ^1H NMR (CD_3OD) δ: 1.30–2.20 (−CH_2−); 2.22–2.98 (=CH−) ppm. ^{13}C NMR (CD_3OD) δ: 35.99; 42.60; 178.68 ppm.

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