# Synthesis of a Novel Polymeric Perfluoro-oxa-alkane Diacyl Peroxide. A Convenient Tool for the Introduction of the Perfluoro-oxa-alkylene Unit

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A new polymeric perfluoro-oxa-alkane diacyl peroxide was prepared by the reaction of the corresponding perfluoro-oxa-alkane diacid fluoride and hydrogen peroxide, and this peroxide was shown to be useful for the introduction of the perfluoro-oxa-alkylene unit into acrylic acid oligomers.

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In perfluoroalkylated polymers, the perfluoroalkyl groups ($F[CF_2]n$–) are usually introduced *via* ester bonds, and these materials are in general unstable because of the presence of the ester moieties. New methods for direct perfluoroalkylation with carbon–carbon bond formation to give perfluoroalkylated polymers are thus required.[1] Recently, we demonstrated that fluoroalkanoyl peroxides $\{(R_FCO_2)_2;\ R_F = F[CF_2]_n$ or $C_3F_7O[CF(CF_3)CF_2O]_mCF(CF_3);\ n = 1, 3, 6, 7, m$ $0, 1, 2\}$ are convenient tools for the introduction of fluoroalkyl groups into various substrates such as aromatic and olefinic compounds.[2] In particular, perfluoro-oxa-alkylated compounds prepared by the use of perfluoro-oxa-alkanoyl peroxides $[\{C_3F_7O[CF(CF_3)CF_2O]_mCF(CF_3)CO_2\}_2]$ have been shown to possess unique properties: extremely low surface tension, and novel biological activity not shown by the corresponding perfluoroalkylated compounds.[2] During our studies on the reactivity of fluoroalkanoyl peroxides, which is different from that of non-fluorinated alkanoyl peroxides,[3] we were interested in preparing new polymeric perfluoro-oxa-alkane diacyl peroxides since their decomposition behaviour and applications have hitherto been unexplored. We have studied the synthesis and reactivity of such compounds and now describe our results.

The polymeric perfluoro-oxa-alkane diacyl peroxide $-[C(:O)R_FC(:O)OO]_p-$(P-FPO) was prepared by the reaction of the corresponding perfluoro-oxa-alkane diacid fluoride and hydrogen peroxide in $CF_2ClCFCl_2$ under alkaline conditions as in eqn. (1).† The IR spectra of P–FPO showed the

$$p\,FC(:O)R_FC(:O)F + p\,H_2O_2 \xrightarrow{OH^-} \underset{\text{P–FPO}}{-[C(:O)R_FC(:O)OO]_p-} \quad (1)$$

$$-R_F- = -(CF_3)CF[OCF_2(CF_3)CF]_n-O[CF_2]_5O-[CF(CF_3)CF_2O]_mCF(CF_3)- \quad (n + m = 3)$$

characteristic diacyl peroxide carbonyl bands at 1857 and 1828 $cm^{-1}$. The thermal decomposition of P–FPO was carried out in $CF_2ClCFCl_2$ at 26–35 °C, and the results are listed in Table 1.

We could not determine the molecular mass of P–FPO owing to its thermal instability; however, its decomposition rates were found to follow closely a first-order equation. The rate constants and activation parameters for the decomposition are similar to those for fluoroalkanoyl peroxides such as $[C_3F_7OCF(CF_3)CO_2]_2$[4] and $(C_7F_{15}CO_2)_2$.[5] These results indicate that P–FPO decomposes with simultaneous homolysis of C–C (carbonyl carbon–fluoroalkyl carbon) and O–O peroxy bonds just as the fluoroalkanoyl peroxides $(R_FCO_2)_2$ which decompose homolytically with decarboxylation to afford $R_F{}^{\bullet}$ radicals,[3,5] and provide a useful means for the introduction of the perfluoro-oxa-alkylene unit (–$R_F$–) into oligomers by a radical process. Hence, radical processes using P–FPO are expected to be the basis for a novel synthetic strategy for the introduction of the perfluoro-oxa-alkylene unit with carbon–carbon bond formation.

The reactions of P–FPO with acrylic acid were examined [eqn. (2)]. To a solution of P–FPO {0.5 mmol [calc. on the basis of the peroxidic monomer unit $-C(:O)R_FC(:O)OO-$ from iodometric titration]} in $CF_2ClCFCl_2$, acrylic acid (28 mmol) was added, and the resulting solution was stirred at 45 °C for 5 h under nitrogen. The white powder obtained was reprecipitated from methanol–ethyl acetate to give the perfluoro-oxa-alkylene unit containing acrylic acid oligomers (1.44 g). This oligomer showed the following data: IR: $\nu/cm^{-1}$ 3080 (OH), 1724 (CO), 1330 ($CF_3$), 1244 ($CF_2$); $^1H$ NMR ($CD_3OD$) δ 1.41–2.11 (–$CH_2$–), 2.26–2.62 (=CH–); $^{19}F$ NMR ($CD_3OD$, ext. $CF_3CO_2H$) δ −3.6 to −8.2 (21F), −46.3 (2F), −49.6 (10F), −69.0 (3F); $^{13}C$ NMR ($CD_3OD$) δ 36.4, 42.9, 178.5; $\bar{M}_n$ = 12 000 ($\bar{M}_w/\bar{M}_n$ = 1.55) (determined by gel permeation chromatography calibration with standard polystyrenes). The results for the reactions of acrylic acid with P–FPO are lised in Table 2.

$$-[C(:O)R_F\,C(:O)OO]_p- + q\ CH_2{=}CHCO_2H \rightarrow -\{R_F-[CH_2-CH(CO_2H)]_q\}_p- \quad (2)$$

As Table 2 shows, these reactions afforded the perfluoro-oxa-alkylene unit containing acrylic acid oligomers in good yields; the molecular masses of the oligomers depended upon the molar ratio of acrylic acid to P–FPO, increasing with higher acrylic acid to P–FPO ratios as is usual for radical oligomerizations. On the other hand, it was found that as the proportion of acrylic acid increased, the content of –$R_F$– units

**Table 1** Thermal decomposition of P–FPO (1% *m/m*)[a] in $CF_2ClCFCl_2$

| $T$/°C | $k_d/10^{-5}\,s^{-1}$ | $\Delta H^{\ddagger}$/kJ mol$^{-1}$ | $\Delta S^{\ddagger}$/J K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|
| 26 | 8.33 ± 0.04 | | |
| 30 | 14.73 ± 0.52 | 91.6 | −16.7 |
| 35 | 25.27 ± 0.85 | | |
| 30 | 11.8[b] | 98.3 | 32.3 |
| 30 | 19.6[c] | 100.0 | 13.8 |

[a] The concentration of the peroxide was determined by iodometric titration. [b] $(C_7F_{15}CO_2)_2$. [c] $[C_3F_7OCF(CF_3)CO_2]_2$; cited in ref. 3.

**Table 2** Synthesis of acrylic acid oligomers containing the perfluoro-oxa-alkylene unit

| | | $-\{R_F-[CH_2-CH(CO_2H)]_q\}_p-$ | | |
|---|---|---|---|---|
| mmol of $CH_2$= $CHCO_2H$ | Acrylic acid/ P–FPO (mol/mol) | Yield (%)[a] | $\bar{M}_n(\bar{M}_w/\bar{M}_n)$ | Content of –$R_F$– unit (%, *m/m*)[b] |
| 14 | 28 | 67 | 9 900 (1.89) | 8 |
| 28 | 56 | 58 | 12 000 (1.55) | 7 |
| 35 | 117 | 77 | 13 100 (1.51) | 3 |
| 150 | 300 | 78 | 26 300 (1.34) | 2 |

[a] The yields are based on the starting materials, acrylic acid and the decarboxylated peroxide unit (–$R_F$–). [b] Content of –$R_F$– unit in oligomer was determined by $^{19}F$ NMR spectroscopy by comparison of the peak area of the $CF_3$ groups of the oligomer with that of benzotrifluoride as the internal standard.

decreased from 8 to 2% (*m*/*m*). If each oligomerization in Table 2 proceeded in 100% yield, the corresponding theoretical –$R_F$– unit contents would become 32, 19, 10, and 4% (*m*/*m*). Thus, the –$R_F$– unit was introduced into acrylic acid oligomers in moderate yield.

The oligomers containing the perfluoro-oxa-alkylene unit are soluble in solvents such as water, methanol, ethanol and tetrahydrofuran. The surface properties of these oligomers were evaluated by measuring the reduction of surface tension of aqueous solutions by the fluorinated oligomer ($\bar{M}_n$ 12 000) using the Du Nöuy ring method. A significant decrease in the surface tension of water to 33.5 mN m$^{-1}$ was observed for a 1 g dm$^{-3}$ solution of this oligomer. In comparison, the surface tension of water was reduced to 20.3 and 53.0 mN m$^{-1}$ for a 1 g dm$^{-3}$ solution of a perfluoro-oxa-alkylated acrylic acid oligomer containing two perfluoro-oxa-alkyl end-groups:[6,7] $R_F$–[$CH_2CH(CO_2H)$]$_n$–$R_F$; $R_F = C_3F_7OCF(CF_3)$ ($\bar{M}_n = 12 000$), which was obtained by the oligomerization of acrylic acid with the corresponding $(R_FCO_2)_2$, and for a solution of commercially available polyacrylic acid, respectively. These values suggest that the perfluoro-oxa-alkylene chains in –[$R_F$–[$CH_2CH(CO_2H)$]$_q$}$_p$– are not likely to be arranged regularly above the water surface compared with the perfluoro-oxa-alkyl chains in $R_F$–[$CH_2CH(CO_2H)$]$_n$–$R_F$.

Thus, polymeric perfluoro-oxa-alkane diacyl peroxide is a useful precursor for the novel introduction of perfluoro-oxa-alkylene units into organic molecules. This method should be widely applicable for the synthesis of molecules partially containing perfluoro-oxa-alkylene units; convenient methods have not hitherto been available for the direct introduction of fluoroalkyl groups for preparing such molecules.

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## Footnote

† The solution of P–FPO in $CF_2ClCFCl_2$ thus obtained was used without further purification and the concentration of P–FPO was determined by iodometry.

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