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Synthesis and Surface Properties of Perfluoro-oxa-alkylated Oligomers

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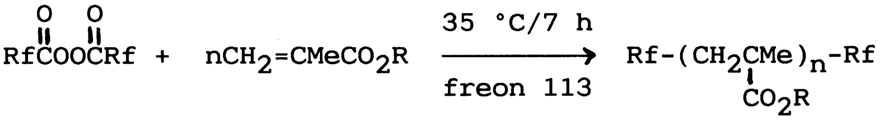
New perfluoro-oxa-alkylated oligomers were obtained by the reactions of methacrylate monomers with perfluoro-oxa-alkanoyl peroxides under very mild conditions, and the perfluoro-oxa-alkylated oligomers containing hydroxyl ethylene oxide units were found to indicate surface properties typical of the amphipathic compounds.

It has been well known that acrylated or methacrylated polymers containing perfluoroalkyl groups exhibit excellent physical and thermal properties , low surface-properties.1) Usually, perfluoroalkyl groups are introduced into polymers through the ester bond, and these materials are in general unstable under acid or alkaline conditions owing to the ester moieties. Therefore, it is much interesting to explore the novel synthetic method for the direct fluoroalkylation into these compounds. Recently, we have demonstrated that fluoroalkanoyl peroxides, especially perfluoro-oxa-alkanoyl peroxides [$(RfCO_2)_2$, Rf = $C_3F_7O\{CF(CF_3)CF_2O\}_mCF(CF_3)$, m = 0, 1, 2] are useful reagents for the introduction of perfluoro-oxa-alkyl groups into aromatic compounds,2) vinyl-,3) or allylsilanes,4) and perfluoro-oxa-alkylated compounds have various unique properties such as extreme decrease of surface tension 5) and biological activity6) which cannot be achieved by the corresponding perfluoroalkylated ones. Perfluoro-oxa-alkanoyl peroxides were also shown to be an excellent precusor for the generation of perfluoro-oxa-alkyl radical.7) So, the perfluoro-oxa-alkanoyl peroxides are expected to be convenient tools for the synthesis of fluoroalkylated materials with carbon-carbon bond formation via radical processes. In this communication, we would like to report the novel synthesis of perfluoro-oxa-alkylated oligomers using perfluoro-oxa-alkanoyl peroxides and the surface properties of these new oligomers.



$$\mathrm{Rf}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Rf} + n\mathrm{CH_2{=}CMeCO_2R} \xrightarrow[\text{freon 113}]{35\ ^\circ\mathrm{C}/7\ \mathrm{h}} \mathrm{Rf\text{-}(CH_2}\underset{\mathrm{CO_2R}}{\mathrm{CMe}}\mathrm{)}_n\mathrm{\text{-}Rf}$$

R = Me [MMA]
= $(CH_2CH_2O)_mH$; m = 1, 2, 4, 5 [PEG-m]

A typical procedure for the synthesis of perfluoro-oxa-alkylated oligomers is as follows. Perfluoro-2-methyl-3-oxa-hexanoyl peroxide (2 mmol) in freon 113 ($CF_2ClCFCl_2$) solution(20 g) was added into the mixture of methyl methacrylate(MMA; 60 mmol) and freon 113(20 g). The solution was stirred at 35 °C for 7 h under nitrogen, and the resulting white powder was reprecipitated from methyl alcohol-chloroform to give perfluoro-1-methyl-2-oxa-pentylated oligomer(2.4g). This oligomer showed the following spectral data: IR(cm^{-1}) 1733(C=O), 1330(CF_3), 1240(CF_2); ^{19}F NMR($CDCl_3$ ext. CF_3CO_2H) δ -5.13 - -6.27(16F), -53.20(6F); ^1H NMR($CDCl_3$) δ 0.70 - 1.15(3H), 1.65 - 2.20(2H), 3.60(3H); average molecular weight ($\overline{Mn}$) = 13600, $\overline{Mw}/\overline{Mn}$ = 1.74 [determined by gel permeation chromatography (GPC) calibrated with standard polystyrenes]. The results for the reactions of MMA or PEG-m with the peroxides are listed in Table 1.

As Table 1 shows, the reactions of MMA with peroxides proceeded smoothly to afford perfluoro-oxa-alkylated oligomers in excellent to moderate yields. The molecular weight of the obtained oligomers were found to be sensitive to the molar ratio of MMA/peroxide, and to become higher ($\approx$13000) with increase of the molar ratio of MMA. Furthermore, contact angles in Table 1 reveal that the surface of perfluoro-oxa-alkylated MMA oligomers exhibits good water- and oil repellency comparing with that of non-fluoroalkylated methyl methylacrylate polymer.
Perfluoro-oxa-alkylated MMA and PEG-m oligomers were able to dissolve the usual organic solvents except for the case of the PEG-1.

In the reactions of methacrylate monomers containing hydroxyl groups (PEG-m) with the peroxides, hydroxyl group containing perfluoro-oxa-alkylated oligomers were obtained under simlar conditions as shown in Table 1. We have already reported that perfluoroalkanoyl peroxide reacts with hydroxyl group containing substrates such as methyl alcohol to suffer the transesterification as the following scheme.[8)]

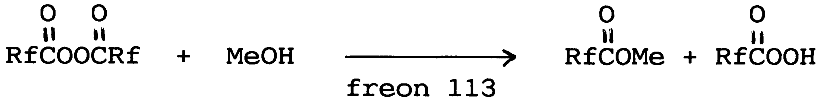
Table 1. Synthesis of Rf-$(CH_2CMeCO_2R)_n$-Rf and Contact Angles of Water and Dodecane on Treated Glass with Rf-$(CH_2CMeCO_2R)_n$-Rf

Peroxide	MMA(PEG-m) Molar ratio	Rf-$(CH_2CMeCO_2R)_n$-Rf		Contact angle (Degree)	
Rf(mmol)	[MMA(PEG-m)/Peroxide]	Yield/%a)	Mn(Mw/Mn)	Water	Dodecane
$CF(CF_3)OC_3F_7$(10)	MMA(10)	91	1300(1.13)	98	49
$CF(CF_3)OC_3F_7$(2)	MMA(20)	86	3900(1.48)	96	43
$CF(CF_3)OC_3F_7$(2)	MMA(30)	34	13600(1.74)	84	20
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$(10)	MMA(30)	26	13300(1.30) [52100(1.66)]b)	98 (72)b)	31 (7)b)
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$(240)	PEG-1(2)	30	——		
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$(240)	PEG-2(1)	40	1500(1.09)	58	61
$CF(CF_3)OC_3F_7$(130)	PEG-1(2)	34	——		
$CF(CF_3)OC_3F_7$(10)	PEG-2(1)	40	1200(1.02)	55	47
$CF(CF_3)OC_3F_7$(10)	PEG-4,5c)(1)	45	1400(1.04)	5	46

a) Yield are based on the starting materials{MMA (PEG-m) and the decarboxylated peroxide unit(Rf-Rf)}.

b) Commercially available methyl methacrylate polymer was used.

c) PEG-4,5 indicates the mixture of tetramer and pentamer of ethylene oxide units.



$$\mathrm{Rf}\overset{O}{\overset{\|}{C}}\mathrm{O}\overset{O}{\overset{\|}{C}}\mathrm{Rf} + \mathrm{MeOH} \xrightarrow[\text{freon 113}]{} \mathrm{Rf}\overset{O}{\overset{\|}{C}}\mathrm{OMe} + \mathrm{Rf}\overset{O}{\overset{\|}{C}}\mathrm{OOH}$$

However, in the reactions with PEG-m, we were able to observe not the similar transesterification as methyl alcohol, but the simple oligomerization to afford the perfluoro-oxa-alkylated oligomers containing hydroxyl group. The different reactivities between PEG-m and methyl alcohol would be correlated with the sites of the HOMO electron densities in these compounds. In fact, the higher electron density in HOMO orbital of PEG-1 was found at not the same hydroxyl position as methyl alcohol but the vinyl one by the MNDO-PM3 semiempirical MO method.$^{9)}$ So, an interaction between SOMO(Rf•) and HOMO(PEG-m) should determine the radical addition of Rf•, which produced by the decomposition of the peroxide, to the vinyl group in PEG-m to afford the corresponding oligomers. Some of the oligomeric products could contain only one perfluoro-oxa-alkylated end-group per molecule(assuming free radical additions with $Mw/Mn \geq 1.02$).

The surface behavior of perfluoro-oxa-alkylated PEG-m oligomers in Table 1 is of particular interest because the contact angles of these oligomers, especially that of the PEG-4,5, exhibit strong hydrophilic property, though these oligomers possess the fluoroalkyl groups. Thus, they are expected to become typical of new fluorinated amphipathic compounds.

In this paper, perfluoro-oxa-alkanoyl peroxides were shown to be useful for the synthesis of perfluoro-oxa-alkylated oligomers, particularly the introduction of perfluoro-oxa-alkyl groups into the oligomers containing the hydroxyl ethylene oxide units with carbon-carbon bond formation. This method is widely applicable for the synthesis of perfluoro-oxa-alkylated oligomers owing to lacking for the convenient method for the direct introduction of fluoroalkyl groups into these oligomers. Further studies are in progress.

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