polymer communication

Synthesis and properties of novel fluoroalkylated allyl alcohol oligomers

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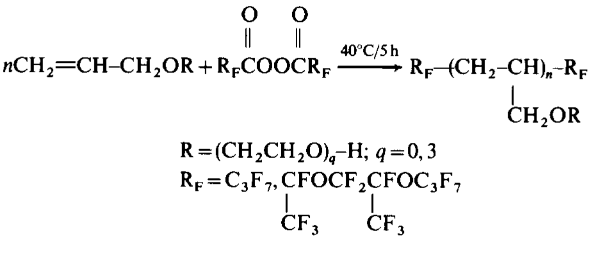
Allyl alcohol and allyl alcohol containing the polyoxyethylene unit were found to react with fluoroalkanoyl peroxides to afford the corresponding fluoroalkylated allyl alcohol oligomers via a radical process under very mild conditions. In particular, fluoroalkylated allyl alcohol oligomers containing the polyoxyethylene unit were shown to be effective in reducing the surface tension of water, and to be applicable for new non-ionic fluorinated amphiphiles.

(Keywords: fluoroalkylated; allyl alcohol oligomers; radical process)

It is well known that allyl compounds such as allylbenzene and allyl acetate are not suitable as radical polymerizable monomers owing to their degradative chain transfer[1]. From such a viewpoint, studies of the radical polymerization of allyl compounds have previously been limited except for a report on the homopolymerization of monoallylammonium salts with a radical initiator containing an azo group[2]. Therefore, it is very interesting to explore the novel initiating systems for these allyl monomers. We have been studying the reactivities of a series of fluoroalkanoyl peroxides [$(R_FCOO)_2$; R_F = perfluoroalkyl, perfluoro-oxaalkyl], which are useful reagents for the introduction of fluoroalkyl groups into arenes or alkenes[3,4]. Very recently, we have developed this fluoroalkylation with peroxides to synthesize acrylic acid and vinyl alcohol oligomers containing fluoroalkylated end groups[5-7]. It is of considerable interest to apply these fluoroalkanoyl peroxides as a novel radical initiating system for allylic monomers. Fluoroalkylated allyl compounds, which would be derived from the reactions of allylic monomers with fluoroalkanoyl peroxides, are expected to receive attention as new functional organofluorinated materials in various fields owing to the lack of convenient methods for the direct introduction of fluoroalkyl groups into allyl compounds. As part of our continuing studies, we reacted fluoroalkanoyl peroxides with allyl alcohol and polyoxyethylene unit containing allyl alcohol (useful functional groups such as the hydroxy group and the polyoxyethylene unit were involved) and these reactions were found to afford the corresponding fluoroalkylated allyl alcohol oligomers via a radical process under very mild conditions. The results are described in this communication.

The various fluoroalkylated allyl alcohol oligomers were synthesized by the reactions of fluoroalkanoyl peroxides with allyl alcohol or polyoxyethylene unit containing allyl alcohol at 40°C for 5 h under nitrogen. The reaction scheme is as follows:



$$n\mathrm{CH_2{=}CH{-}CH_2OR} + \mathrm{R_F\overset{\overset{\displaystyle O}{\|}}{C}OO\overset{\overset{\displaystyle O}{\|}}{C}R_F} \xrightarrow{40^\circ\mathrm{C}/5\,\mathrm{h}} \mathrm{R_F{-}(CH_2{-}\underset{\underset{\displaystyle CH_2OR}{|}}{CH})_{\mathit{n}}{-}R_F}$$

$$\mathrm{R} = \mathrm{(CH_2CH_2O)_{\mathit{q}}{-}H};\ q = 0, 3$$

$$\mathrm{R_F} = \mathrm{C_3F_7},\ \mathrm{\underset{\underset{\displaystyle CF_3}{|}}{C}FOCF_2\underset{\underset{\displaystyle CF_3}{|}}{C}FOC_3F_7}$$

The fluoroalkylated allyl alcohol oligomers thus obtained were identified by i.r., ^{1}H n.m.r. and ^{19}F n.m.r. spectroscopic analysis, as well as by g.p.c. analysis (calibrated with standard polystyrenes). For example, the allyl alcohol oligomer ($R_F = C_3F_7$, R = H) shows the following spectral data: i.r.(ν, cm^{-1}) 3430(OH), 1350(CF_2), 1223(CF_2); ^{1}H n.m.r.($CDCl_3$) δ 1.18–2.81 (CH_2, CH), 3.20–4.62 (CH_2); ^{19}F n.m.r.($CDCl_3$, ext. CF_3CO_2H) δ −3.8 (6F), −43.0 (4F), −51.0 (4F); $\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$) = 900 (1.34).

As shown in *Table 1*, both perfluoropropylated and perfluoro-oxaalkylated allyl alcohol oligomers were obtained in excellent to moderate yields under very mild conditions, though allyl alcohol or polyoxyethylene unit containing allyl alcohol possesses a reactive hydroxy

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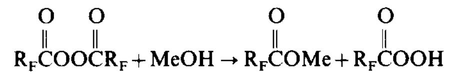
Table 1 Reactions of fluoroalkanoyl peroxides with allyl alcohols

R_F in peroxide (mmol)	R in allyl alcohol (mmol)	Yield (%)[a]	$\bar{M}_n (\bar{M}_w/\bar{M}_n)$
C_3F_7(10)	H(20)	51	900(1.34)
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$(10)	H(20)	62	1130(1.52)
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$(10)	H(40)	53	1160(1.60)
C_3F_7(10)	$(CH_2CH_2O)_3H$(40)	32	1070(1.60)
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$(10)	$(CH_2CH_2O)_3H$(20)	89	1440(1.08)
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$(10)	$(CH_2CH_2O)_3H$(40)	85	1140(1.30)

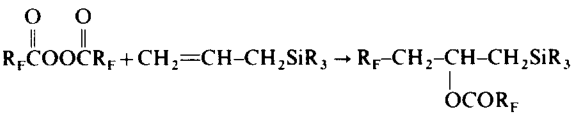
[a] The yields were based on the starting materials [allyl alcohols and the decarboxylated peroxide unit (R_F-R_F)]

group. We have already reported that perfluoroalkanoyl peroxide reacts with hydroxy group containing substrates such as methyl alcohol to undergo transesterification as in the following scheme[8]:



$$R_F\overset{O}{\overset{\|}{C}}O O\overset{O}{\overset{\|}{C}}R_F + MeOH \rightarrow R_F\overset{O}{\overset{\|}{C}}OMe + R_F\overset{O}{\overset{\|}{C}}OOH$$

However, in the reactions of fluoroalkanoyl peroxides with allyl alcohols, we did not observe a transesterification as for methyl alcohol, but a simple oligomerization to afford fluoroalkylated oligomers containing the hydroxy group. The different reactivities between allyl alcohols and methyl alcohol may be correlated with the sites of the HOMO electron densities in these compounds. In fact, the higher electron density in the HOMO orbital was not found at the same hydroxy position as in methyl alcohol but rather at the terminal carbon position ($CH_2{=}CH{-}CH_2{-}OR$) in allyl alcohols by the MNDO-PM3 semiempirical MO method with the MOPAC 5.0 program[9]. Since fluoroalkyl radicals are in general electrophilic due to the high electronegativity of fluorine, an interaction between SOMO ($R_F\cdot$) and HOMO (allyl alcohols) should determine the radical addition of $R_F\cdot$, produced by the decomposition of the peroxide, to the terminal olefinic position in allyl alcohols to afford the corresponding oligomers. On the other hand, in the reactions of allylic organosilicon compounds such as allylsilanes with fluoroalkanoyl peroxides, we have found that these reactions proceed not by a radical process but a single electron transfer from the HOMO of allylsilanes to the antibonding O–O bond (LUMO) of peroxides to give 1:1 adducts in good yields[10]:



$$R_F\overset{O}{\overset{\|}{C}}O O\overset{O}{\overset{\|}{C}}R_F + CH_2{=}CH{-}CH_2SiR_3 \rightarrow R_F{-}CH_2{-}\underset{\underset{OCOR_F}{|}}{CH}{-}CH_2SiR_3$$

Thus, the reactions of fluoroalkanoyl peroxides with allyl alcohol and allylsilanes gave quite different reaction products. The HOMO energy levels of allyl alcohol and trimethoxyallylsilane have been calculated using the MNDO-PM3 semiempirical MO method[9]. Allyl alcohol was shown to have a considerably lower HOMO energy level (−10.074 eV) than that for trimethoxyallylsilane (−9.193 eV)*. So, a weaker interaction between the HOMO energy level of allyl alcohol and LUMO (peroxide) causes a new interaction between HOMO (allyl alcohol) and SOMO of the fluoroalkyl radical ($R_F\cdot$) in contrast with the case of a strong interaction between HOMO (trimethoxyallylsilane) and LUMO (peroxide) resulting in a single electron transfer from trimethoxyallylsilane to the peroxide. Hence, an interaction between SOMO ($R_F\cdot$) and HOMO (allyl alcohol) should determine the addition of a fluoroalkyl radical ($R_F\cdot$) to allyl alcohol, thus affording the corresponding oligomers in excellent to moderate yields. In our present oligomeric condition, as shown in *Table 1*, the concentration of fluoroalkanoyl peroxide is higher than that of allyl alcohol compared with that of the usual radical polymerization, so an oligomer with two fluoroalkyl fragments would be obtained via a primary radical termination of the growing radicals with the radical produced by the decomposition of peroxide, or via a chain transfer to the peroxide.

Interestingly, these fluoroalkylated allyl alcohol oligomers were found to be soluble in common organic solvents such as methanol, ethanol, tetrahydrofuran, carbon tetrachloride, chloroform, ethyl acetate, benzene, toluene, dimethyl sulfoxide and *N*,*N*-dimethylformamide, and they were even soluble in water. In general, fluorinated surfactants such as perfluoroalkyl acrylate polymers are known to have poor solubility in various solvents except for fluorinated solvents. However, our fluoroalkylated oligomers were found to have good solubility in various solvents, and to be useful for novel fluorinated allylic amphiphiles. The surfactant properties of the fluorinated allyl alcohol oligomers were evaluated by surface tension measurements of their aqueous solutions with the Wilhelmy plate method at 25°C. For example, a significant decrease in the surface tension of water ($72.3\,mN\,m^{-1}$) to $23.3\,mN\,m^{-1}$ was observed for a $2\,g\,dm^{-3}$ solution of $R_F{-}(CH_2{-}CHCH_2OR)_n{-}R_F$ [$R_F = C_3F_7$, $R = (CH_2CH_2O)_3H$].

Thus, our fluoroalkylated oligomers are expected to be widely applicable for novel fluoroalkylated allylic amphiphiles owing to the lack of a convenient method of preparation of fluoroalkylated allylic compounds. Further investigations of the synthesis and properties of a series of fluoroalkylated allylic oligomers are now in progress.

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* Previously, we reported that styrene or ethyl vinyl ether reacts with perfluoroalkanoyl peroxides to give 1:1 adducts by a single electron transfer from styrene (or ethyl vinyl ether) to the peroxides, whereas trimethoxyvinylsilane or methyl methacrylate reacts with the peroxides to give the corresponding fluoroalkylated oligomers via a radical process. The HOMO energy levels of these substrates with the MOPAC 6.01 program are as follows: styrene, −9.132 eV; ethyl vinyl ether, −9.459 eV; trimethoxyvinylsilane, −9.864 eV; methyl methacrylate, −10.522 eV (see ref. 4)

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