Synthesis and properties of fluoroalkylated vinyl alcohol oligomers

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New fluoroalkylated vinyl alcohol oligomers were prepared by the alcoholysis of the corresponding fluoroalkylated vinyl acetate oligomers, which were obtained by the reactions of fluoroalkanoyl peroxides with vinyl acetate. These vinyl alcohol oligomers exhibited a quite different solubility from non-fluorinated poly(vinyl alcohol).

(Keywords: vinyl alcohol oligomers; solubility; contact angles)

Introduction

Poly(vinyl alcohol) is a hydrophilic material that has been widely used in various fields. From the synthetic and practical point of view, the modification of this material is of particular interest. The surface hydrophobing of poly(vinyl alcohol) film was carried out in the gas phase by treating with saturated carbonyl chlorides having long alkyl or perfluoroalkyl chains[1,2]. In continuation of our systematic investigations of fluoroalkanoyl peroxides[3–5], we were interested in preparing new fluoroalkylated vinyl alcohol oligomers with fluoroalkanoyl peroxides. We found that fluoroalkylated vinyl alcohol oligomers [R_F–$(CH_2CHOH)_n$–R_F; $R_F = C_3F_7$, $CF(CF_3)[OCF_2CF(CF_3)]_mOC_3F_7$; $m = 0, 1$] were prepared under mild conditions by the alcoholysis of the corresponding fluoroalkylated vinyl acetate oligomers, which were obtained by the reactions of fluoroalkanoyl peroxides [$(R_FCO_2)_2$] with vinyl acetate, and these oligomers showed not hydrophilic but oleophilic properties. These results are described in this communication.

Fluoroalkylated vinyl acetate oligomers [**1**: R_F–$(CH_2CHOAc)_n$–R_F; $R_F = C_3F_7$, $CF(CF_3)[OCF_2CF(CF_3)]_mOC_3F_7$; $m = 0, 1$] were prepared by the reactions of fluoroalkanoyl peroxides with vinyl acetate in trichlorotrifluoroethane, at 45°C for 5 h under nitrogen, in 21–39% isolated yields. The concentrations of fluoroalkanoyl peroxides used were higher than that of vinyl acetate (molar ratio of vinyl acetate/peroxides = 20–30), in contrast to the usual case for radical polymerization. Under these conditions mainly vinyl acetate oligomers with two fluoroalkyl groups would be obtained via primary radical termination or radical chain transfer to the peroxide, as well as by our previously reported method[6,7] for the synthesis of fluoroalkylated acrylic acid oligomers having two fluoroalkyl end-groups in one oligomeric molecule [R_F–$(CH_2CHCO_2H)_n$–R_F]. However, it was suggested that some of the fluoroalkylated vinyl acetate oligomers contained only one fluoroalkylated end-group per molecule, as indicated in *Table 1* ($\bar{M}_w/\bar{M}_n > 1$). We succeeded in obtaining a series of fluoroalkylated vinyl alcohol oligomers (**2**) from the corresponding vinyl acetate oligomers in excellent to moderate yields by methanolysis containing hydrogen chloride under reflux conditions, although fluoroalkylated vinyl alcohol oligomers (**2**) were isolated by methanolysis of the corresponding fluoroalkylated vinyl acetate oligomers under alkaline conditions in very low yields. The above-mentioned reaction scheme is as follows.

$$R_FCOOCR_F + nCH_2{=}CHOAc \rightarrow R_F\text{–}(CH_2CHOAc)_n\text{–}R_F \quad \mathbf{1}$$

$$\xrightarrow[\text{reflux}]{\text{HCl/MeOH}} R_F\text{–}(CH_2CHOH)_n\text{–}R_F \quad \mathbf{2}$$

$R_F = C_3F_7$, $CF(CF_3)[OCF_2CF(CF_3)]_mOC_3F_7$, $m = 0, 1$

Each obtained fluoroalkylated vinyl alcohol oligomer was purified by reprecipitation from a methanol/water system, and identified by i.r., ^{1}H n.m.r., ^{19}F n.m.r. and g.p.c. analyses. For example, perfluoropropylated vinyl alcohol oligomer exhibited the following spectral data: i.r. (cm^{-1}) 3450 (OH), 1353 (CF_3), 1228 (CF_2); ^{1}H n.m.r. (CD_3OD) δ 1.02–2.01 (–CH_2–), 3.81–4.81 (=CH–); ^{19}F n.m.r. (CD_3OD) δ −4.1 (CF_3), −37.2 (CF_2), −51.5 (CF_2); $\bar{M}_n = 5900$ ($\bar{M}_w/\bar{M}_n = 1.37$). The i.r. spectra of fluoroalkylated vinyl alcohol oligomers thus obtained

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Table 1 Synthesis of fluoroalkylated vinyl alcohol oligomers, $[R_F\text{-}(CH_2CHOH)_n\text{-}R_F]$, and contact angles for water and dodecane on the glass treated with $R_F\text{-}(CH_2CHOH)_n\text{-}R_F$

R_F in $R_F\text{-}(CH_2CHOAc)_n\text{-}R_F$					$R_F\text{-}(CH_2CHOH)_n\text{-}R_F$		
						Contact angle (degree)	
	$\bar{M}_n$	$(\bar{M}_w/\bar{M}_n)$	Weight (g)	Yield[a] (%)	$\bar{M}_n$ $(\bar{M}_w/\bar{M}_n)$	Water	Dodecane
C_3F_7	6700	(2.07)	12.6	67	5900 (1.37)	77	53
$CF(CF_3)OC_3F_7$	8000	(2.36)	8.97	66	7600 (1.29)	101	60
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	4500	(1.92)	15.8	53	3800 (1.54)	106	72
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	5400	(1.92)	12.6	22	4800 (1.52)	104	69
							22[b]
						49[c]	0[c]

[a] Molar yields based on the fluoroalkylated vinyl acetate oligomers
[b] Poly(vinyl alcohol): degree of polymerization 1750; degree of hydrolysis 88.0 mol%. We were not able to measure the contact angle of water owing to poly(vinyl alcohol) film being soluble in water
[c] Untreated glass

showed the characteristic hydroxyl band at around 3450 cm^{-1}, but did not completely show the characteristic carbonyl band at around 1740 cm^{-1}, which appeared in the corresponding vinyl acetate oligomers. The molecular weights and isolated yields of a series of fluoroalkylated vinyl alcohol oligomers are listed in *Table 1*.

Interestingly, fluoroalkylated vinyl alcohol oligomers were shown to exhibit a good solubility for common organic solvents such as chloroform, methanol, ethanol, tetrahydrofuran, ethyl acetate, dimethylformamide and dimethylsulfoxide. In general, poly(vinyl alcohol)s are well known to be soluble in water but not in organic solvents; however, our vinyl alcohol oligomers were found to be completely insoluble in water. We measured the contact angles for water and dodecane on the glass treated with these oligomers, and the results are shown in *Table 1*. As *Table 1* shows, the contact angles for water and dodecane on the treated glass were found to increase significantly, indicating that these oligomers (in particular, oligomers having perfluoro-oxa-alkyl chains) possess good water- and oil-repellent properties.

Thus, our fluoroalkylated vinyl alcohol oligomers were shown to confer good water-repellent and lipophobic properties and to demonstrate a quite different solubility from the parent poly(vinyl alcohol). Further investigations of the synthesis and properties of a series of fluoroalkylated vinyl alcohol oligomers are now in progress.

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