Synthesis and Properties of Novel Fluoroalkyl End-Capped Oligomers Containing Phosphorus Segments

HIDEO SAWADA,[1] DAISUKE TAMADA,[1] TOKUZO KAWASE,[2] YOSHIO HAYAKAWA,[3] KYUNGHO LEE,[4] JUN KYOKANE,[4] MASANORI BABA[5]

[1] Department of Chemistry, Nara National College of Technology, Yamatokoriyama, Nara 639-1080, Japan

[2] Faculty of Human Life Science, Osaka City University, Sumiyoshi, Osaka 558-8585, Japan

[3] National Industrial Research Institute of Nagoya, Kita, Nagoya 462-8510, Japan

[4] Department of Electrical Engineering, Nara National College of Technology, Yamatokoriyama, Nara 639-1058, Japan

[5] Division of Human Retroviruses, Center for Chronic Viral Diseases, Faculty of Medicine, Kagoshima University, Sakuragaoka, Kagoshima 890-8520 Japan

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ABSTRACT: New fluoroalkyl end-capped oligomers containing pendant phosphoric acid groups were prepared by the reactions of the corresponding monomer with fluoroalkanoyl peroxides. It was demonstrated that not only strong aggregations of fluoroalkyl segments but also hydrogen bonding could interact synergistically to form the highly viscoelastic fluids (gel-like fluids) in aqueous solutions of these new fluoroalkyl end-capped oligomers containing pendant phosphoric acid groups. Furthermore, these oligomers were able to reduce the surface tension of water effectively to exhibit a clear breakpoint resembling a CMC, and the modified stainless-steel surface treated with these oligomers was shown to possess an excellent property imparted by fluorine. More interestingly, these oligomers were found to be potent and selective inhibitors against HIV-1 replication *in vitro*. New fluoroalkyl end-capped phosphonic acid and phosphonate oligomers were also prepared by the reactions of the corresponding phosphonic acid and phosphonate monomers, respectively, by the use of fluoroalkanoyl peroxides. These new fluoroalkyl end-capped phosphonic acid and phosphonate oligomers were found to have a higher solubility in not only water but also in common organic solvents than that of the corresponding fluorinated oligomers containing pendant phosphoric acid groups, and these new oligomers were able to reduce the surface tension of these solvents quite effectively. Thus, these oligomers are expected to develop as new fluorinated oligosurfactants. Moreover, the modified poly(methyl methacrylate) surface treated with these phosphonate oligomers was clarified to exhibit a good oil-repellency imparted by fluorine. In addition, fluoroalkyl end-capped phosphonate homo- and cooligomers were found to form monomolecular films at the air–water interface. Therefore, these fluorinated oligomers are suggested to have high potential for new functional materials through not only their excellent properties imparted by both fluorine and

Correspondence to: H. Sawada.

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phosphorus, but also through their biological properties. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 228–245, 2001

Key words: fluorinated oligomer; end-capped fluoroalkyl; phosphorus segment; surface tension; contact angle; anti-HIV-1 activity; fluoroalkanoyl peroxide

INTRODUCTION

Recently, the increasing importance of organofluorine compounds in applications for new functional materials has led to considerable interest in the synthesis of organofluorine compounds containing phosphorus atoms.[1] In particular, these fluorinated phosphorous compounds have attracted considerable attention in chemistry and biochemistry from the viewpoints of applications such as surfactants, flame-retardant materials, electrolytes, and biological chelating agents.[2] In fact, various monofluorinated and fluoroalkylated phosphorous compounds have been prepared, and their interesting properties have been reported.[3] Furthermore, in the fluorinated polymers containing phosphorus segments, Burton et al. reported on the synthesis and applications of perfluorocarbon polymers containing phosphonic acid groups.[4] Hitherto, we have been actively studying the synthesis and applications of partially fluorinated macromolecules such as acrylic acid oligomers containing two fluoroalkyl endgroups. Interestingly, these partially fluorinated polymers were found to exhibit various unique properties such as a good solubility in various solvents and a surface-active property which cannot be achieved by the usual fluorinated macromolecules.[5] More interestingly, it was clarified that these fluorinated oligomers, especially fluorinated oligomers containing carboxy and sulfo segments, can form the intra- or intermolecular aggregates, which are constructed by aggregations of the end-capped fluoroalkyl segments in aqueous solutions to exhibit a selective anti-HIV-1 activity *in vitro*.[6,7] Therefore, it is very interesting to synthesize novel partially fluorinated polymeric compounds containing phosphorus segments in order to open a new route to the development of the field of new functional materials imparted by both fluorine and phosphorus. In preliminary communications, we found that novel fluoroalkyl end-capped oligomers containing pendant phosphoric acid groups are prepared by use of fluoroalkanoyl peroxides and these fluorinated oligomers possess a selective anti-HIV 1 activity *in vitro*.[8] We now give a full account of the synthesis and properties of fluoroalkyl end-capped oligomers containing phosphorus segments.

EXPERIMENTAL

NMR spectra were measured using a Varian Unityplus 500 (500-MHz) spectrometer, while IR spectra were recorded on a HORIBA FT-300 FTIR spectrophotometer. Molecular weights were calculated using a Shodex DS-4 (pomp) and Shodex RI-71 (detector) gel permeation chromatography (GPC) calibrated with standard polystyrenes [or poly(ethylene glycol)] using tetrahydrofuran (THF) [or a 30% acetonitrile solution containing 0.2*M* AcOH and 0.2*M* AcONa, 0.2*M* Na_2HPO_4, 0.4*M* Na_2HPO_4 and 1*M* NaCl solution containing 50 mM $H_2NC(CH_2OH)_3$] as the eluent. The surface tensions of an aqueous solution of fluoroalkyl end-capped oligomers containing phosphorus segments were measured at 30°C using a Wilhelmy-type surface tensiometer (ST-1, Shimadzu Co.) with a glass plate. Surface pressure–molecular area isotherms were measured by the moving-wall method using a Nippon Laser & Electronics Lab. NL-LB240S-MWA apparatus. The contact angles were measured using a goniometer-type contact angle meter (ERMA G-1-1000) according to our previously reported method.[9]

Materials

A series of fluoroalkanoyl peroxides were prepared from the corresponding acyl halides and hydrogen peroxide in aqueous sodium hydroxide according to our method previously reported.[10] Methacrylate monomers containing pendant phosphoric acid (PEM) and phosphoric acid monoethanolamine segments (MPE) were supplied by the Yuni Chemical Co., Ltd. (Nara, Japan). Vinylphosphonic acid (VPA) and diethyl vinylphosphonate (DEVP) were purchased from the Sigma–Aldrich Japan Co., Ltd.. (Tokyo, Japan). Dimethylacrylamide (DMAA) and acrylorylmorpholine (ACMA) were supplied by the Cohjin Co., Ltd. (Tokyo, Japan). Acrylic acid was purchased

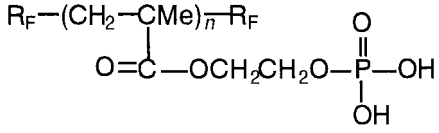
from Wako Pure Chemical Industries Ltd. (Osaka, Japan).

General Procedure for the Synthesis of Fluoroalkyl End-capped Oligomers Containing Phosphorus Segments

Perfluorobutyryl peroxide (4 mmol) in 1:1 mixed solvents (AK-225) of 1,1-dichloro-2,2,3,3,3-pentafluoropropane-1,3-dichloro-1,2,2,3,3-pentafluoropropane (68 g) was added to the aqueous solution (10%, w/w) of the methacrylate monomer containing a pendant phosphoric acid group {8 mmol, PEM [2-(methacryloyloxy)ethyl phosphate]}. The heterogeneous solution was stirred vigorously at 40°C for 5 h under nitrogen. Methanol was added to the reaction mixture and the solvent evaporated under reduced pressure. The crude product obtained was reprecipitated from methanol–ethyl acetate to give bis(perfluoropropylated)methacrylate oligomers containing pendant phosphoric acid groups (0.70 g). This oligomer showed the following spectral data:

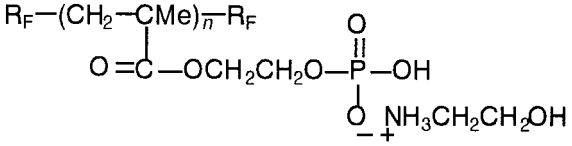
IR ν/cm^{-1} 3472(OH), 1718(C═O), 1330(CF_3), 1230(CF_2), 983(P—O); ^{1}H-NMR(D_2O) δ 0.72–1.48(CH_3), 1.77–2.14(CH_2), 4.01–4.25(CH_2); ^{19}F-NMR(D_2O, ext. CF_3CO_2H) δ −5.09(6F), −43.20 (4F), −52.26(4F).

Similarly, a series of fluoroalkyl end-capped oligomers containing PEM and MPE and fluoroalkyl end-capped VPA cooligomers were prepared using fluoroalkanoyl peroxides. These exhibited the following spectral characteristics:



R_F = $C_3F_7OCF(CF_3)$: IR(ν/cm^{-1}) 3421(OH), 1720(C═O), 1350(CF_3), 1257(CF_2), 1027(P—O); ^{1}H-NMR(D_2O) δ 0.58–1.22(CH_3), 1.42–2.21(CH_2), 3.42–4.38(CH_2); ^{19}F-NMR(D_2O, ext. CF_3CO_2H) δ −6.96(16F), −53.82(6F).

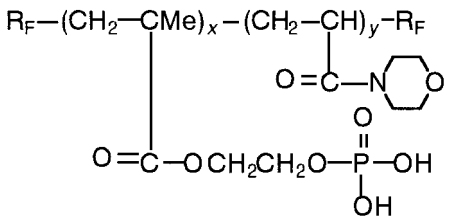
R_F = $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$: IR($\nu/cm^{-1}$) 3517(OH), 1716(C═O), 1350(CF_3), 1252(CF_2), 986(P—O); ^{1}H-NMR(D_2O) δ 0.59–1.31(CH_3), 1.70–2.12(CH_2), 3.80–4.28(CH_2); ^{19}F-NMR(D_2O, ext. CF_3CO_2H) δ −6.93(26F), −53.79(6F), −68.56(2F).



R_F = C_3F_7: IR(ν/cm^{-1}) 3471(OH), 1726(C═O), 1371(CF_3), 1267(CF_2), 978(P—O); ^{1}H-NMR(D_2O) δ 0.58–1.25(CH_3), 1.52–2.14(CH_2), 2.94–3.25(CH_2), 3.58–3.90(CH_2), 3.92–4.36(CH_2); ^{19}F-NMR(D_2O, ext. CF_3CO_2H) δ −4.70(6F), −43.04(4F), −52.78(4F).

R_F = $C_3F_7OCF(CF_3)$: IR(ν/cm^{-1}) 3470(OH), 1724(C═O), 1345(CF_3), 1240(CF_2), 984(P—O); ^{1}H-NMR(D_2O) δ 0.62–2.22(CH_3, CH_2), 2.95–3.15(CH_2), 3.58–3.75(CH_2), 3.80–4.42(CH_2); ^{19}F-NMR(D_2O, ext. CF_3CO_2H) δ −7.79(16F), −54.65(6F).

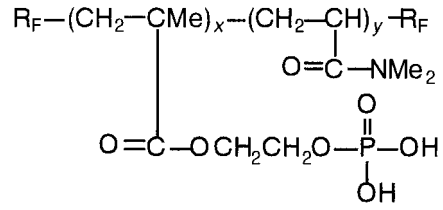
R_F = $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$: IR($\nu/cm^{-1}$) 3349(OH), 1726(C═O), 1320(CF_3), 1241(CF_2), 991(P—O); ^{1}H-NMR(D_2O) δ 0.38–2.18(CH_3, CH_2), 2.86–3.28(CH_2), 3.64–3.88(CH_2), 3.90–4.28(CH2); ^{19}F-NMR(D_2O, ext. CF_3CO_2H) δ −8.13(26F), −56.15(6F), −70.95(2F).



R_F = C_3F_7: IR(ν/cm^{-1}) 3448(OH), 1722(C═O), 1622(C═O), 1320(CF_3), 1242(CF_2), 984(P—O); ^{1}H-NMR(D_2O) δ 0.60–2.14(CH_3, CH_2), 2.32–2.91(CH), 3.22–3.81(CH_2), 3.91–4.26(CH_2); ^{19}F-NMR(D_2O, ext. CF_3CO_2H) δ −5.56(6F), −43.04(4F), −52.10(4F).

R_F = $C_3F_7OCF(CF_3)$: IR(ν/cm^{-1}) 3446(OH), 1728(C═O), 1631(C═O), 1348(CF_3), 1254(CF_2), 1028(P—O); ^{1}H-NMR(D_2O) δ 0.68–2.12(CH_3, CH_2), 2.38–2.86(CH), 3.15–4.29(CH_2); ^{19}F-NMR(D_2O, ext. CF_3CO_2H) δ −6.93(16F), −54.03(6F).

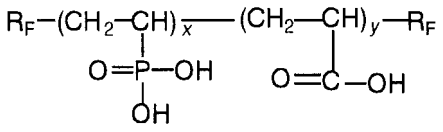
R_F = $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$: IR($\nu/cm^{-1}$) 3490(OH), 1728(C═O), 1616(C═O), 1246(CF2), 986(P—O); ^{1}H-NMR(D_2O) δ 0.65–1.20(CH_3), 1.39–1.86(CH_2), 2.25–2.92 (CH), 3.28–4.25(CH_2); ^{19}F-NMR(D_2O, ext. CF_3CO_2H) δ −6.86(26F), −54.26(6F), −56.04(2F).



R_F = $C_3F_7OCF(CF_3)$: IR(ν/cm^{-1}) 3429(OH), 1728 (C═O), 1618(C═O), 1242(CF2), 999(P—O); ^{1}H-NMR(D_2O) δ 0.68–2.03(CH_3, CH_2), 2.42–3.25(CH,

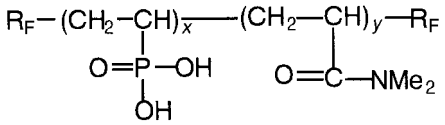
CH_3), 3.72–4.39(CH_2); ^{19}F-NMR(D_2O, ext. CF_3CO_2H) δ −7.37(16F), −54.91(6F).

R_F = $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$: IR($\nu$/cm^{-1}) 3408(OH), 1726(C═O), 1618(C═O), 1345(CF_3), 1244(CF_2), 996(P—O); ^{1}H-NMR(D_2O) δ 0.58–2.12(CH_3, CH_2), 2.32–3.30(CH, CH_3), 3.41–4.32 (CH_2); ^{19}F-NMR(D_2O, ext. CF_3CO_2H) δ −8.05(26F), −56.05(6F), −70.69(2F).



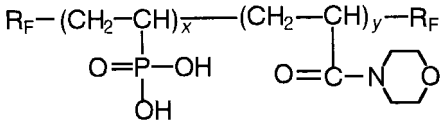
R_F = $C_3F_7OCF(CF_3)$: IR(ν/cm^{-1}) 3400(OH), 1720(C═O), 1340(CF_3), 1250(CF_2), 1150(P═O), 1050(P—O); ^{1}H-NMR(D_2O) δ 1.24–1.87(CH_2), 2.06–2.43(CH), 2.43–2.78(CH); ^{19}F-NMR(D_2O, ext. CF_3CO_2H) δ −5.91(16F), −57.28(6F)

R_F = $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2OCF(CF_3)$: IR($\nu$/cm^{-1}) 3430(OH), 1720(C═O), 1310(CF_3), 1240(CF_2), 1150(P═O), 1000(P—O); ^{1}H-NMR(D_2O) δ 1.03–1.90(CH_2), 2.21–2.39(CH), 2.39–2.75(CH); ^{19}F-NMR(D_2O, ext. CF_3CO_2H) δ −8.47(36F), −60.02(6F), −75.22(4F).



R_F = $C_3F_7OCF(CF_3)$: IR(ν/cm^{-1}) 3350(OH), 1620(C═O), 1500(CON), 1320(CF_3), 1250(CF_2), 1150(P═O), 1000(P—O); ^{1}H-NMR(D_2O) δ 1.11–1.88(CH_2), 2.28–3.15(CH, CH_3); ^{19}F-NMR(D_2O, ext. CF_3CO_2H) δ −7.76(16F), −57.28(6F).

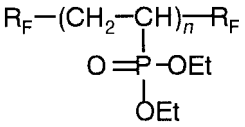
R_F = $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2OCF(CF_3)$: IR($\nu$/cm^{-1}) 3420(OH), 1610(C═O), 1500(CON), 1300(CF_3), 1250(CF_2), 1150(P═O), 1000(P—O); ^{1}H-NMR(D_2O) δ 1.01–1.89(CH_2), 2.28–2.98(CH, CH_3); ^{19}F-NMR(D_2O, ext. CF_3CO_2H) δ −6.78(36F), −57.88(6F), −75.92(4F).



R_F = $C_3F_7OCF(CF_3)$: IR(ν/cm^{-1}) 3400(OH), 1620 (C═O), 1450(CON), 1310(CF_3), 1240(CF_2), 1150(P═O), 1030(P—O); ^{1}H-NMR(D_2O) δ 1.13–2.00(CH_2), 2.32–2.76(CH), 3.01–3.77(CH_2); ^{19}F-NMR(D_2O, ext. CF_3CO_2H) δ −8.06(16F), −57.28(6F).

R_F = $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2OCF(CF_3)$: IR($\nu$/cm^{-1}) 3400(OH), 1630(C═O), 1440(CON), 1300(CF_3), 1240(CF_2), 1110(P═O), 1020(P—O); ^{1}H-NMR(D_2O) δ 0.98–1.8 (CH_2), 2.20–2.77(CH), 3.21–3.76(CH_2); ^{19}F-NMR(D_2O, ext. CF_3CO_2H) δ −8.32(36F), −59.28(6F), −74.36(4F).

A typical experiment for the synthesis of fluoroalkyl end-capped DEVP oligomers is as follows: A solution of perfluorobutyryl peroxide (3.2 mmol) in 1:1 mixed solvents (AK-225) of 1,1-dichloro-2,2,3,3,3-pentafluoropropane-1,3-dichloro-1,2,2,3,3-pentafluoropropane (45 g) was added to DEVP (8.7 mmol). The solution was stirred at 40°C for 5 h under nitrogen. After the solvent was evaporated, the obtained crude product was dialyzed to give the bis(perfluoropropylated) DEVP oligomer. This oligomer showed the following spectral data:



R_F = C_3F_7: IR(ν/cm^{-1}) 1305(CF_3), 1230(CF_2), 1210(P═O), 1030(P—O); ^{1}H-NMR($CDCl_3$) δ 0.92–3.30(CH_2, CH), 1.16–1.48(CH_3), 4.02–4.24(CH_2); ^{19}F-NMR($CDCl_3$, ext. CF_3CO_2H) δ −4.78(6F), −44.47(4F), −52.08(4F).

Other fluoroalkyl end-capped DEVP oligomers were obtained under similarly mild conditions. The following spectral data were obtained for the other products studied:

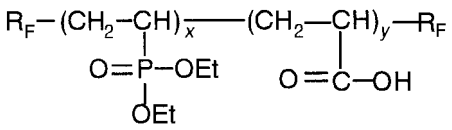
R_F = $C_3F_7OCF(CF_3)$: IR(ν/cm^{-1}) 1330(CF_3), 1240(CF_2), 1210(P═O), 1030(P—O); ^{1}H-NMR($CDCl_3$) δ 0.99–3.20 (CH_2, CH), 1.11–1.42(CH_3), 4.00–4.25(CH_2); ^{19}F-NMR($CDCl_3$, ext. CF_3CO_2H) δ −6.80(16F), −53.95(6F).

R_F = $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$: IR($\nu$/cm^{-1}) 1310($CF_3$), 1220(CF2), 1200(P═O), 1040(P—O); ^{1}H-NMR($CDCl_3$) δ 1.12–305(CH_2, CH), 1.21–1.38 (CH_3), 4.02–4.22(CH_2); ^{19}F-NMR($CDCl_3$, ext. CF_3CO_2H) δ −5.87(26F), −54.13(6F), −69.94(2F).

R_F = $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2OCF(CF_3)$: IR($\nu$/cm^{-1}) 1310($CF_3$), 1240($CF_2$), 1210(P═O), 1050(P—O); ^{1}H-NMR($CDCl_3$) δ 1.12–3.09 (CH_2, CH), 1.22–1.41(CH_3), 4.01–4.22(CH_2); ^{19}F-NMR ($CDCl_3$, ext. CF_3CO_2H) δ −7.03(36F), −54.26(6F), −69.63(4F).

A series of fluoroalkyl end-capped DEVP cooligomers were obtained under similarly mild con-

ditions and the obtained products were purified by dialysis or reprecipitation. The following spectral data were obtained for these fluorinated cooligomers studied:

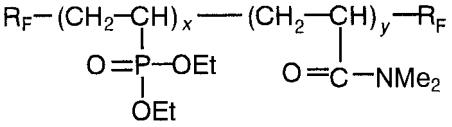


R_F = C_3F_7: IR(ν/cm^{-1}) 3200(OH), 1710(C═O), 1310(CF_3), 1220(CF_2), 1190(P═O), 1030(P—O); ^{1}H-NMR(D_2O) δ 1.12–1.22(CH_3), 1.22–3.00(CH_2, CH), 4.02–4.31(CH_2); ^{19}F-NMR(D_2O, ext. CF_3CO_2H) δ −5.22(6F), −40.77(4F), −55.93(4F)

R_F = $C_3F_7OCF(CF_3)$: IR(ν/cm^{-1}) 3210(OH), 1730(C═O), 1350(CF_3), 1270(CF_2), 1210(P═O), 1030(P—O); ^{1}H-NMR(D_2O) δ 0.89–2.81 (CH_2, CH), 1.12–1.22(CH_3), 4.08–4.31(CH_2); ^{19}F-NMR (D_2O, ext. CF_3CO_2H) δ −6.96(16F), −53.95(6F).

R_F = $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$: IR($\nu$/cm^{-1}) 3200(OH), 1720(C═O), 1320(CF_3), 1260(CF_2), 1170(P═O), 1020(P—O); ^{1}H-NMR(D_2O) δ 0.92–2.95(CH_2, CH), 1.05–1.21(CH_3), 34.09–4.22(CH_2); ^{19}F-NMR(D_2O, ext. CF_3CO_2H) δ −7.89(26F), −56.05(6F), −70.61(2F).

R_F = $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2OCF(CF_3)$: IR($\nu$/cm^{-1}) 3210(OH), 1740(C═O), 1305(CF_3), 1250(CF_2), 1160(P═O), 1020(P—O); ^{1}H-NMR(D_2O) δ 0.87–2.95(CH_2, CH), 1.05–1.22(CH_3), 4.08–4.33 (CH_2); ^{19}F-NMR(D_2O, ext. CF_3CO_2H) δ −8.53(36F), −59.60(6F), −75.26(4F).

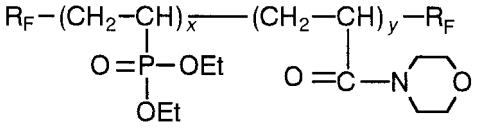


R_F = C_3F_7: IR(ν/cm^{-1}) 1640(C═O), 1500(CON), 1354(CF_3), 1230(CF_2), 1170(P═O), 1030(P—O); ^{1}H-NMR($CDCl_3$) δ 0.95–3.42(CH_2, CH, CH_3), 1.22–1.48(CH_3), 4.01–4.41(CH_2); ^{19}F-NMR($CDCl_3$, ext. CF_3CO_2H) δ −5.55(6F), −46.73(4F), −54.88(4F).

R_F = $C_3F_7OCF(CF_3)$: IR(ν/cm^{-1}) 1650(C═O), 1500(CON), 1350(CF_3), 1240(CF_2), 1150(P═O), 1030(P—O); ^{1}H-NMR($CDCl_3$) δ 1.00–3.68(CH_2, CH, CH_3), 1.20–1.41(CH_3), 4.00–4.22(CH_2); ^{19}F-NMR($CDCl_3$, ext. CF_3CO_2H) δ −7.10(16F), −57.64(6F).

R_F = $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$: IR($\nu$/cm^{-1}) 1630(C═O), 1390(CON), 1310(CF_3), 1240(CF_2), 1200(P═O), 1040(P—O); ^{1}H-NMR($CDCl_3$) δ 1.05–3.28(CH_2, CH, CH_3), 1.22–1.41(CH_3), 4.02–4.25 (CH_2); ^{19}F-NMR($CDCl_3$, ext. CF_3CO_2H) δ −6.16 (26F), −57.50(6F), −74.29(2F).

R_F = $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2OCF(CF_3)$: IR($\nu$/cm^{-1}) 1680(C═O), 1400(CON), 1300(CF_3), 1240(CF_2), 1200(P═O), 1050(P—O); ^{1}H-NMR($CDCl_3$) δ 0.92–3.22(CH_2, CH, CH_3), 1.22–1.41 (CH_3), 4.00–4.25(CH_2); ^{19}F-NMR($CDCl_3$, ext. CF_3CO_2H) δ −4.80(36F), −57.64(6F), −74.21(4F).



R_F = C_3F_7: IR(ν/cm^{-1}) 1640(C═O), 1450(CON), 1358(CF_3), 1230(CF_2), 1120(—O—), 1030(P—O); ^{1}H-NMR(D_2O) δ 0.82–2.75(CH_2, CH), 1.18–1.35 (CH_3), 3.02–3.82(CH_2), 3.92–4.15(CH_2); ^{19}F-NMR (D_2O, ext. CF_3CO_2H) δ −5.91(6F), −45.82(4F), −55.48(4F).

R_F = $C_3F_7OCF(CF_3)$: IR(ν/cm^{-1}) 1630(C═O), 1440(CON), 1320(CF_3), 1220(CF_2), 1100(—O—), 1040(P—O); ^{1}H-NMR(D_2O) δ 0.98–2.00(CH_2), 1.10–1.38(CH_3), 2.34–2.70(CH), 3.09–3.89(CH_2), 3.92–4.10(CH_2); ^{19}F-NMR(D_2O, ext. CF_3CO_2H) δ −8.17(16F), −57.55(6F).

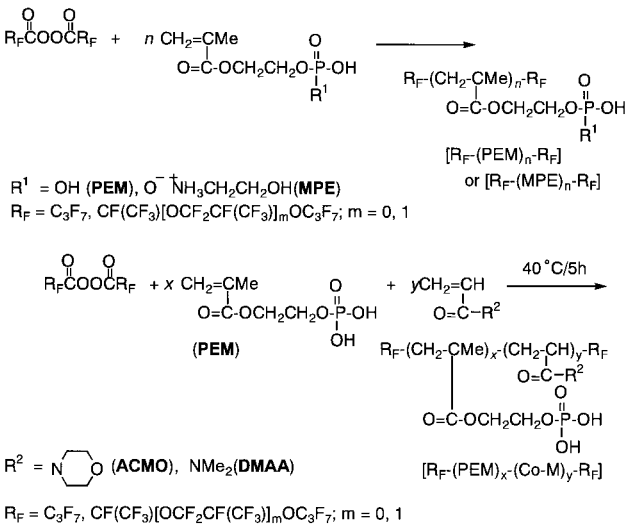
R_F = $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$: IR($\nu$/cm^{-1}) 1640(C═O), 1430(CON), 1300(CF_3), 1230(CF_2), 1110(—O—), 1040(P—O); ^{1}H-NMR(D_2O) δ 0.88–2.09(CH_2), 1.08–1.28(CH_3), 2.35–2.70(CH), 3.10–3.80(CH_2), 3.90–4.08(CH_2); ^{19}F-NMR(D_2O, ext. CF_3CO_2H) δ −8.17(26F), −59.21(6F), −74.95 (2F).

R_F = $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2OCF(CF_3)$: IR($\nu$/cm^{-1}) 1630(C═O), 1420(CON), 1300(CF_3), 1240(CF_2), 1110(—O—), 1030(P—O); ^{1}H-NMR (D_2O) δ 0.85–2.06(CH_2), 1.08–1.25(CH_3), 2.36–2.68(CH), 3.10–3.85(CH_2), 3.90–4.09(CH_2); ^{19}F-NMR(D_2O, ext. CF_3CO_2H) δ −8.48(36F), −59.60 (6F), −75.20(4F).

RESULTS AND DISCUSSION

Synthesis of Fluoroalkyl End-capped Oligomers Containing PEM and MPE

The reactions of fluoroalkanoyl peroxides with the methacrylate monomer (PEM or MPE) were carried out in heterogeneous solvent systems [AK-225 (mixed solvents of 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,3-dichloro-1,2,2,3,3-pentafluoropropane) and water] by stirring



Scheme 1

vigorously at 40°C for 5 h under nitrogen. The process is outlined in Scheme 1.

Table I shows perfluoropropyl and some perfluorooxaalkyl end-capped PEM (or MPE) homooligomers in 10–23% isolated yields under mild conditions. Similarly, in the cooliogomerization of PEM or MPE with fluoroalkanoyl peroxides, we succeeded in preparing a series of fluoroalkyl end-capped PEM or MPE cooligomers by using comonomers such as acryloylmorpholine (ACMO) and dimethylacrylamide (DMAA) in 5–30% isolated yields (see Scheme 1 and Table I).

The cooligomerization ratio of cooligomers in Table I was determined by ^{1}H-NMR analyses. Furthermore, we tried to measure the molecular weight of each oligomer in Table I by GPC analyses. In fact, GPC analyses of R_F–$(PEM)_n$–R_F and R_F–$(PEM)_x$–$(ACMO)_y$–R_F were studied under various conditions, and these results are shown in Table II.

As shown in Table II, we could not measure the molecular weights of homo- and cooligomers by GPC by using 0.2*M* acetic acid and sodium ace-

Table I Synthesis of Fluoroalkylated End-capped Oligomers Containing PEM and MPE by the Use of Fluoroalkanoyl Peroxides

Run	R_F in Peroxide (mmol)	PEM (or MPE) (mmol)	Co-M (mmol)	Product		
				Yield (%)[a]	M_n(M_w/M_n)	[x:y][b]
		PEM			R_F–$(PEM)_n$–R_F	
1	C_3F_7 (4)	8		22	—	
2	$CF(CF_3)OC_3F_7$ (3)	6		14	31000 (1.11)	
3	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (3)	6		10	—	
		MPE			R_F–$(MPE)_n$–R_F	
4	C_3F_7 (4)	8		22	28000 (1.10)	
5	$CF(CF_3)OC_3F_7$ (3)	6		23	—	
6	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (3)	6		18	—	
		PEM	ACMO	R_F–$(PEM)_x$–$(ACMO)_y$–R_F		
7	C_3F_7 (4)	12	20	5	72000 (1.38)	[61:39]
8	$CF(CF_3)OC_3F_7$ (3)	9	15	7	63000 (1.21)	[40:60]
9	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (3)	9	15	11	84000 (1.02)	[35:65]
		MPE	DMAA	R_F–$(MPE)_x$–$(DMAAA)_y$–R_F		
10	$CF(CF_3)OC_3F_7$ (3)	9	9	23	—	[75:25]
11	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (3)	9	9	30	—	[60:40]

[a] The yields were based on the starting materials [PEM (or MPE), ACMO (or DMAA) and the decarboxylated peroxide unit (R_F—R_F)].

[b] Cooligomerization ratio was determined by ^{1}H-NMR.

Table II GPC Analyses of Fluoroalkylated End-capped PEM Homooligomer and PEM–ACMO Cooligomer

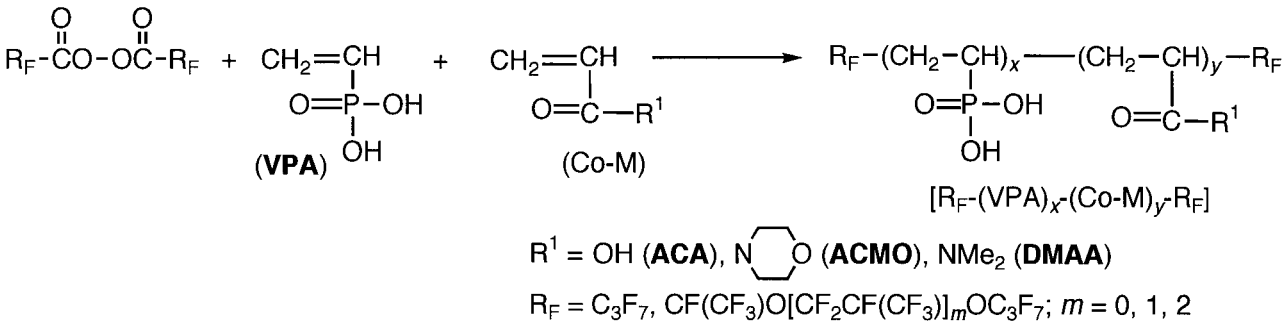
Oligomer	Eluent	$\overline{M_n}$($\overline{M_w}$/$\overline{M_n}$)
R_F–$(PEM)_n$–R_F[a]	0.2*M* AcOH and 0.2*M* AcONa	—
	0.2*M* Na_2HPO_4	52,000 (1.39)
	0.4*M* Na_2HPO_4	67,000 (1.24)
	50 m*M* $H_2NC(CH_2OH)_3$ and 1*M* NaCl	31,000 (1.11)
R_F–$(PEM)_x$–$(ACMO)_y$–R_F[a]	0.2*M* AcOH and 0.2*M* AcONa	—
	0.2*M* Na_2HPO_4	86,000 (1.96)
	0.4*M* Na_2HPO_4	90,000 (1.23)
	50 m*M* $H_2NC(CH_2OH)_3$ and 1*M* NaCl	63,000 (1.21)

[a] R_F = $CF(CF_3)OC_3F_7$.

tate as the eluent. However, by using 0.2–0.4*M* Na_2HPO_4 solutions or a 50 m*M* $H_2NC(CH_2OH)_3$ and 1*M* NaCl solution as the eluent, the molecular weights of these oligomers were measured by GPC analyses. It is well known that a decreasing concentration of a compound, which tends to be associated in solution, results in a lower degree of association. Interestingly, the molecular weights of these oligomers measured by GPC were found to decrease with increasing concentration of the eluents. Considering the fact that water-soluble fluoroalkyl end-capped oligomers such as fluoroalkyl end-capped acrylic acid (ACA) oligomers and ACMO oligomers can easily form molecular aggregates owing to the strong aggregations of end-capped fluoroalkyl segments in aqueous solutions,[11] it is suggested that the obtained values by GPC indicate the apparent molecular weights. In fact, we could measure the molecular weights of some oligomers in Table I by using a 50 m*M* $H_2NC(CH_2OH)_3$ and 1*M* NaCl solution as the eluent. However, we could not measure the molecular weights of other oligomers in Table I by GPC analyses under various conditions. This result strongly suggests that not only the strong aggregations of fluoroalkyl segments but also the hydrogen-bonding interaction between phosphoric acid (or phosphoric acid monoethanolamine) segments in aqueous solutions of fluorinated oligomers could interact synergistically to form the highly viscoelastic fluids (gel-like fluids). In fact, it was shown that the oligomers, which cannot be measured by their molecular weights (nos. 1, 3, 5, 6, 10, and 11), are mixed with water to form easily the gel-like fluids. In contrast, we were able to measure easily the molecular weights of the corresponding nonfluorinated PEM polymer [—$(PEM)_n$—: M_n = 21,000 (M_w/M_n = 1.61] and the MPE polymer [—$(MPE)_n$—: M_n = 28,000 (M_w/M_n = 1.30)] by GPC analyses, and these polymers were completely soluble in water.

Synthesis of Fluoroalkyl End-Capped Phosphonic Acid and Phosphonate Oligomers

First, we tried to react fluoroalkanoyl peroxides with VPA to obtain fluoroalkyl end-capped VPA homooligomers. When the reactions of VPA with



Scheme 2

Table III Synthesis of Fluoroalkylated End-capped VPA Cooligomers by the Use of Fluoroalkanoyl Peroxides

No.	R_F in Peroxide (mmol)	VPA (mmol)	Co-M (mmol)	Product Yield (%)[a]	Product $\overline{M_n}(\overline{M_w}/\overline{M_n})$ [x:y][b]
	R^1 = OH (ACA)				
12	$CF(CF_3)OC_3F_7$ (3.7)	10	32	41	3900 (1.37) [30:70]
13	$CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (2.0)	5.9	20	20	14,300 (2.39) [21:79]
	R^1 = NMe_2 (DMAA)				
14	$CF(CF_3)OC_3F_7$ (3.5)	10	9.8	23	3600 (1.34) [14:86]
15	$CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (2.1)	5.8	5.9	12	5700 (2.34) [11:89]
	R^1 =  (**ACMO**)				
16	$CF(CF_3)OC_3F_7$ (3.5)	9.6	16	17	5400 (1.63) [17:83]
17	$CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (2.1)	5.8	9.9	13	14,700 (3.43) [12:88]

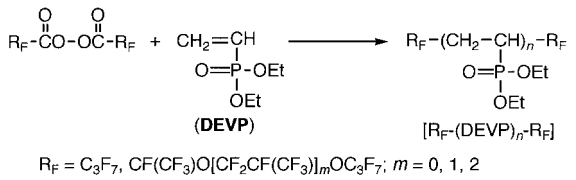
[a] The yields were based on the starting materials [VPA, ACMO (or DMAA, ACA) and the decarboxylated peroxide unit (R_F—R_F)].
[b] Cooligomerization ratio was determined by ^{1}H-NMR.

fluoroalkanoyl peroxides were carried out under heterogeneous conditions including water due to the water-soluble property of VPA, the expected oligomers were not isolated. This finding resulted from both the lower radical polymerizable property of VPA and the heterogeneous conditions. Therefore, in the above reaction system, it is interesting to use higher radical polymerizable monomers such as ACA, ACMO, and DMAA as comonomers. In fact, we succeeded in obtaining fluoroalkyl end-capped VPA cooligomers by using radical polymerizable monomers such as ACA, ACMO, and DMAA as comonomers in the above reaction system as shown in Scheme 2. These results are shown in Table III.

Table IV Synthesis of Fluoroalkylated End-capped Phosphonate Homooligomers by the Use of Fluoroalkanoyl Peroxides

No.	R_F in Peroxide (mmol)	DEVP (mmol)	Product Yield (%)[a]	Product $\overline{M_n}(\overline{M_w}/\overline{M_n})$
18	C_3F_7 (3.2)	8.7	71	2300 (1.06)
19	$CF(CF_3)OC_3F_7$ (3.3)	10	33	1200 (1.10)
20	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (2.5)	7.6	62	2400 (1.06)
21	$CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (1.9)	5.4	88	1200 (1.19)

[a] The yields were based on the starting materials [DEVP and the decarboxylated peroxide unit (R_F—R_F)].



Scheme 3

As shown in Table III, fluoroalkyl end-capped VPA cooligomers were obtained in 12–41% isolated yields under very mild conditions. Interestingly, fluoroalkylated VPA–ACA and VPA–DMAA cooligomers were easily soluble in water, methanol, ethanol, and THF. On the other hand, fluoroalkylated VPA–ACMO cooligomers were found to be soluble not only in water but also in chloroform.

As mentioned above, fluoroalkyl end-capped PEM homo- and cooligomers were shown to form the gel-like fluids in water. However, fluoroalkyl end-capped VPA cooligomers thus obtained were found to be completely soluble in water and polar organic solvents such as MeOH, EtOH, and THF. This finding suggests that since hydroxy segments in fluoroalkyl end-capped VPA cooligomers were directly introduced into the main oligomer chains the intermolecular hydrogen bonding between hydroxy segments cannot participate strongly in the gelator which is constructed by the aggregations of the fluoroalkyl units. In contrast, since hydroxy segments in fluoroalkyl end-capped PEM oligomers were introduced into the main oligomer chains through the ester spacer, the intermolecular hydrogen bonding between hydroxy segments can participate strongly in the gel construction with the aggregation of end-capped fluoroalkyl segments.

Furthermore, we tried to synthesize fluoroalkyl end-capped oligomers containing phosphonate segments using fluoroalkanoyl peroxide as a key intermediate (Table IV). The reactions of DEVP with fluoroalkanoyl peroxides are expected to proceed under a homogeneous system since DEVP has a highly oleophilic property. In fact, as shown in Scheme 3, the reactions of fluoroalkanoyl peroxides with DEVP in AK-225 were found to proceed under a homogeneous system to give the corresponding fluoroalkyl end-capped DEVP homooligomers in 33–88% isolated yields.

Interestingly, these fluoroalkyl end-capped DEVP homooligomers were found to be insoluble in water; however, these homooligomers were easily soluble in common organic solvents including nonpolar organic solvents such as benzene except for hexane. Therefore, these fluorinated DEVP homooligomers are expected to be applied to new oleophilic oligosurfactants.

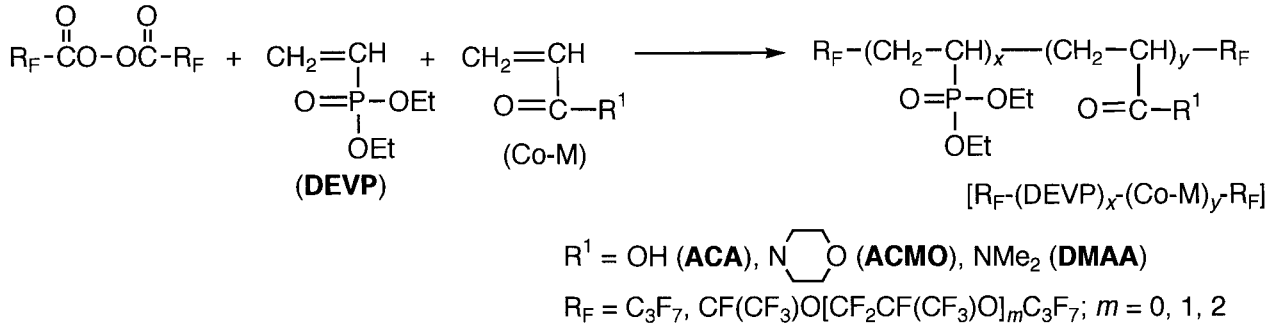
To develop the water-soluble fluorinated phosphonate oligomers, we tried to synthesize fluorinated DEVP cooligomers by using hydrophilic comonomers such as ACA, DMAA, and ACMO.

The cooligomerization of DEVP with fluoroalkanoyl peroxides were found to proceed under mild conditions to give the corresponding fluoroalkylated DEVP cooligomers in excellent-to-moderate isolated yields as shown in Scheme 4 and Table V.

These fluorinated DEVP cooligomers show a good solubility in not only water but also in common organic solvents including nonpolar solvents. Usually, fluorinated materials possess only limited solubility in various solvents,[12] and this remarkable improvement in their solubility is of clear importance from the viewpoints of the development of fluorinated phosphorous materials.

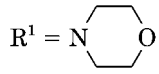
Surfactant Properties of Fluoroalkyl End-capped PEM and MPE Oligomers

Owing to the application of fluoroalkyl end-capped oligomers containing phosphorus seg-



Scheme 4

Table V Synthesis of Fluoroalkylated End-capped DEVP Cooligomers by the Use of Fluoroalkanoyl Peroxides

No.	R_F in Peroxide (mmol)	DEVP (mmol)	Co-M (mmol)	Product Yield (%)[a]	Product $\overline{M_n}(\overline{M_w}/\overline{M_n})$ [x:y][b]
	R^1 = OH (ACA)				
22	C_3F_7 (2.9)	8.8	29	44	800 (1.42) [7:93]
23	$CF(CF_3)OC_3F_7$ (3.4)	10	34	47	1500 (1.04) [7:93]
24	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (2.6)	7.7	25	22	1600 (1.14) [6:94]
25	$CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (1.8)	5.4	18	32	2200 (1.14) [6:94]
	R^1 = NMe_2 (DMAA)				
26	C_3F_7 (3.9)	12	12	53	4600 (1.07) [8:92]
27	$CF(CF_3)OC_3F_7$ (3.3)	10	10	45	4600 (1.16) [11:89]
28	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (2.8)	8.5	8.5	79	4800 (1.37) [11:89]
29	$CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (2.1)	6.0	6.0	83	4900 (1.64) [11:89]
	R^1 =  (**ACMO**)				
30	C_3F_7 (4.1)	12	20	88	3100 (1.13) [6:94]
31	$CF(CF_3)OC_3F_7$ (2.3)	6.5	11	95	3100 (1.12) [6:94]
32	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (2.8)	8.4	14	33	3300 (1.19) [5:95]
33	$CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (2.0)	6.0	10	27	6500 (2.42) [6:94]

[a] The yields were based on the starting materials [DEVP, ACA (or DMAA, ACMO) and the decarboxylated peroxide unit (R_F—R_F)].
[b] Cooligomerization ratio was determined by ^{1}H-NMR.

ments as new phosphorus-containing fluorinated functional materials, it is interesting to evaluate the surface properties of the aqueous solutions of these fluorinated oligomers containing phosphorus segments. We measured the reduction of surface tension of water by these oligomers with the Wilhelmy plate method at 30°C. Surface tensions of aqueous solutions of fluoroalkyl end-capped PEM homo- and cooligomers and MPE oligomers are shown in Figures 1–3, respectively.

As Figures 1 and 2 show, a significant decrease in the surface tension of water, to around 20 mN/m, was found for perfluoro-1-methyl-2-oxapentylated PEM homo- and ACMO cooligomers compared to the corresponding nonfluorinated homooligomer. Furthermore, these fluorinated PEM homo- and cooligomers exhibit a breakpoint resembling a critical micelle concentration (CMC). However, PEM homo- and cooligomers containing longer perfluorooxaalkyl groups [R_F = $CF(CF_3)$-$OCF_2CF(CF_3)OC_3F_7$] were not as effective for re-

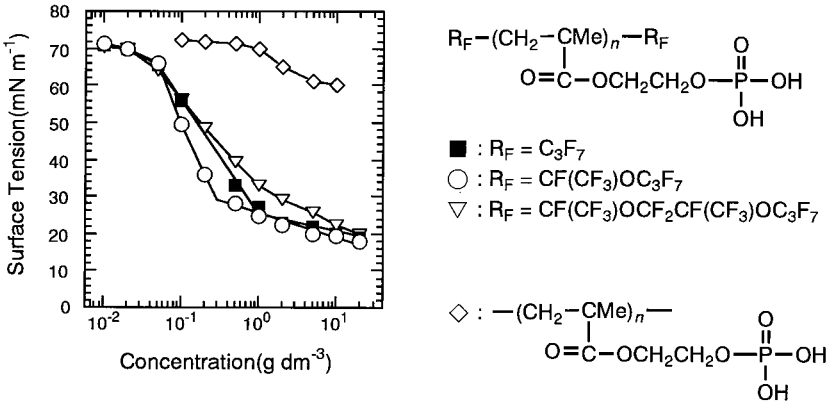


Figure 1 Surface tension of aqueous solutions of phosphoric acid oligomers at 30°C.

ducing the surface tension of water compared to that of the shorter perfluoroxaalkylated [R_F = $CF(CF_3)OC_3F_7$] oligomer. This finding suggests that the longer perfluorooxaalkyl chains in these fluorinated PEM oligomers are unlikely to be arranged more closely above the water surface owing to the steric hindrance of the longer fluoroalkyl chains.

As shown in Figure 3, fluoroalkyl end-capped MPE oligomers were also able to reduce the surface tension of water quite effectively, despite the fact that the corresponding nonfluorinated MPE oligomer was not able to reduce the surface tension of water. Similarly, a shorter perfluorooxaalkylated [R_F = $CF(CF_3)OC_3F_7$] MPE oligomer was more effective for reducing the surface tension of water. Therefore, these fluorinated PEM and MPE homo- and cooligomers are applicable to new fluorinated hydrophilic oligosurfactants containing phosphorus segments.

Surfactant Properties of Fluoroalkyl End-capped VPA Cooligomers

The fluoroalkyl end-capped VPA cooligomers in Scheme 2 exhibit a poor solubility in common organic solvents; however, these VPA cooligomers were found to show a good solubility in water. Thus, we measured the surface tension of aqueous solutions of these VPA cooligomers with the Wilhelmy plate method at 30°C, and the results are shown in Figure 4.

As shown in Figure 4, fluoroalkyl end-capped VPA–ACMO, VPA–DMAA, and VPA–ACA cooligomers were able to reduce the surface tension of water effectively with a clear breakpoint resembling a CMC, the same as for low-molecular weight fluorinated surfactants. Therefore, these cooligomers are expected to be useful for new fluorinated hydrophilic oligosurfactants.

Surfactant Properties and Monolayer Behaviors of Fluoroalkyl End-capped DEVP Oligomers

Fluoroalkyl end-capped DEVP homooligomers and DEVP–ACMO cooligomers, which were prepared by the use of fluoroalkanoyl peroxides, are easily soluble in common organic solvents. Therefore, these DEVP oligomers are expected to be applicable for new fluorinated oleophilic oligosurfactants. Thus, we measured the surface tension

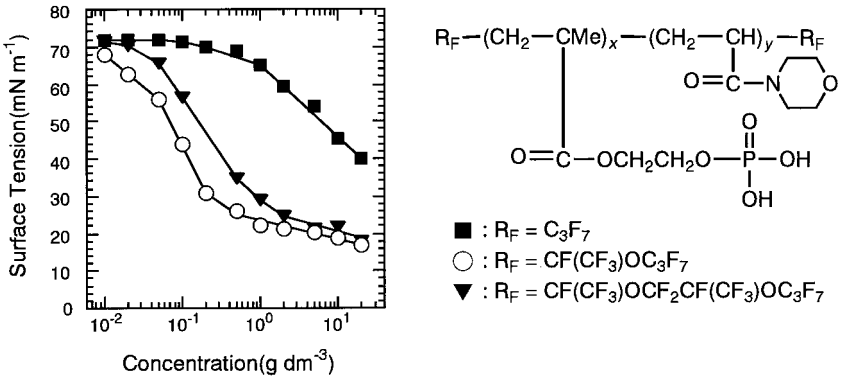


Figure 2 Surface tension of aqueous solutions of phosphoric acid cooligomers at 30°C.

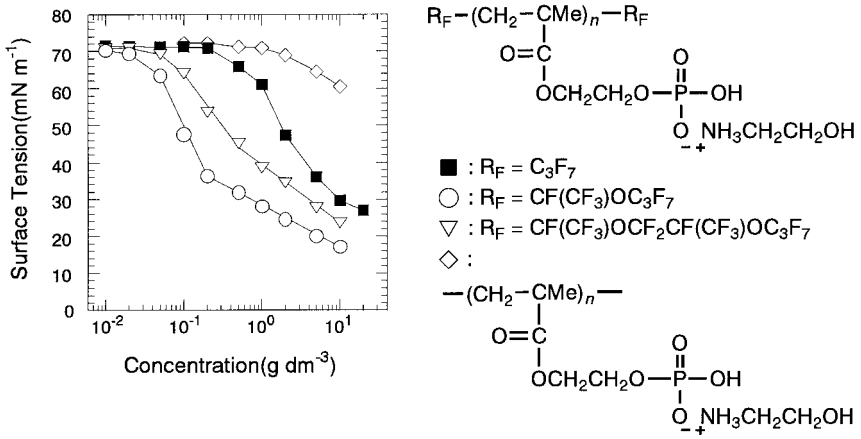


Figure 3 Surface tension of aqueous solutions of R_F–$(MPE)_n$–R_F at 30°C.

of an *m*-xylene solution of these DEVP oligomers with the Wilhelmy plate method at 30°C, and the results are shown in Figures 5 and 6.

As shown in Figure 5, fluoroalkyl end-capped DEVP homooligomers were able to reduce the surface tension of *m*-xylene effectively. Especially, longer perfluorooxaalkyl end-capped DEVP homooligomers were more effective for reducing the surface tension of *m*-xylene to around 15 mN/m levels with a clear breakpoint compared to the corresponding perfluoropropylated, perfluoro-1-methyl-2-oxapentylated, and nonfluorinated oligomers. Similarly, as shown in Figure 6, longer perfluorooxaalkylated DEVP–DMAA cooligomers were effective for reducing the surface tension of *m*-xylene effectively compared to the corresponding shorter fluoroalkylkated and nonfluorinated cooligomers. Thus, our fluorinated, especially longer fluoroalkylated, DEVP homo and cooligomers are interesting materials for new fluorinated oleophilic oligosurfactants.

Fluoroalkyl end-capped DEVP–DMAA cooligomers are also soluble not only in common organic solvents but also in water. Similarly, fluoroalkyl end-capped DEVP–ACA and DEVP–ACMO cooligomers were found to have a good solubility in water and common organic solvents. Therefore, these fluorinated DEVP cooligomers are useful for new fluorinated hydrophilic oligosurfactants. In fact, as shown in Figures 7 and 8, these fluorinated DEVP cooligomers were able to reduce the surface tension of water quite effectively with a clear breakpoint resembling a CMC compared to the corresponding nonfluorinated cooligomers.

Hitherto, it has been well known that polysoaps in which fluoroalkyl groups have been introduced randomly into polymeric molecules possess a low solubility in various solvents and are not effective for reducing the surface tension of water.[13] In addition, these randomly fluoroalkylated polysoap solutions have no CMC or break-

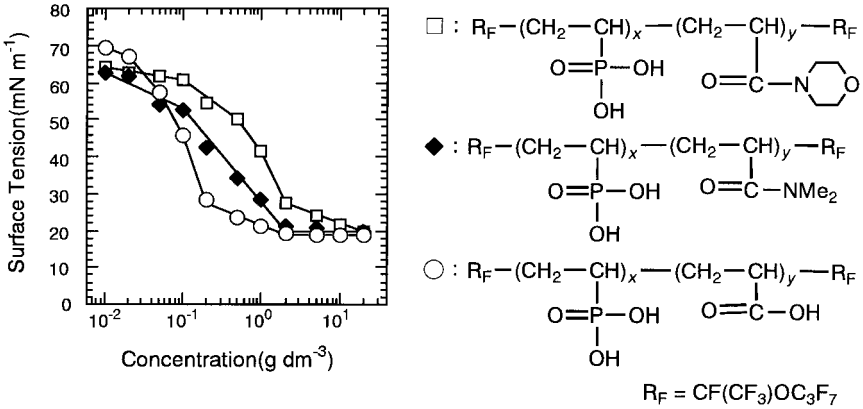


Figure 4 Surface tension of aqueous solutions of R_F–$(VPA)_x$–$(Co\text{-}M)_y$–R_F at 30°C.

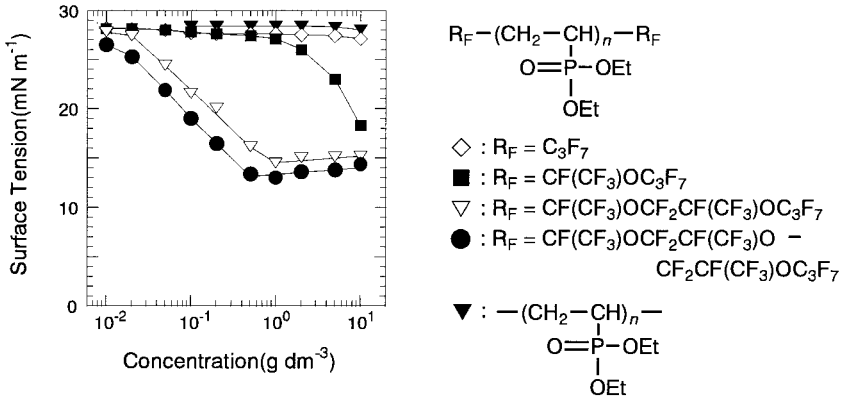


Figure 5 Surface tension of *m*-xylene of R_F–(DEVP)$_n$–R_F at 30°C.

point resembling a CMC.[13] In this respect, our present fluoroalkyl end-capped oligomers containing phosphorus segments could develop as novel fluorinated oligosurfactants possessing a high solubility and a surface-active property into various fields.

In this way, fluoroalkyl end-capped oligomers containing phosphorus segments, especially fluorinated DEVP homo- and cooligomers, were found to indicate surfactant properties typical of the amphiphilic compounds. Therefore, it is very interesting to study the formation of stable monolayers of these fluorinated DEVP oligomers at the air/water interface by the Langmuir–Blodgett method. In fact, a chloroform solution of each fluorinated DEVP oligomer was spread on the water surface, and the surface pressure–surface area (π-A) isotherm was measured. The π-A isotherm of each oligomer on pure water is shown in Figures 9 and 10.

As shown in Figures 9 and 10, perfluoropropyl end-capped DEVP homooligomer and DEVP–ACA cooligomers were found to form not only as expanded film in a lower surface pressure region, which indicates that the fluoroalkyl groups are parallel with the water surface, but also a condensed film in a higher surface pressure. The transition point between the two states for the fluorinated DEVP homooligomer is in the vicinity of 5 mN/m. Similarly, each fluoroalkylated DEVP–ACA cooligomer has the transition point between the two states, and it was clarified that the values for the transition points become higher with longer fluoroalkyl groups in cooligomers. The limiting areas of these cooligomers at zero pressure (π_0) were found to become larger with increasing of their molecular weights as in Figure 10. The π_0 values of these cooligomers, which are structurally reasonable, suggest that the fluoroalkyl groups are perpendicular to the water surface and closed packed to each other.

On the other hand, as shown in Figure 9, longer fluoroalkyl (except for perfluoropropyl) end-capped DEVP homooligomers were found to

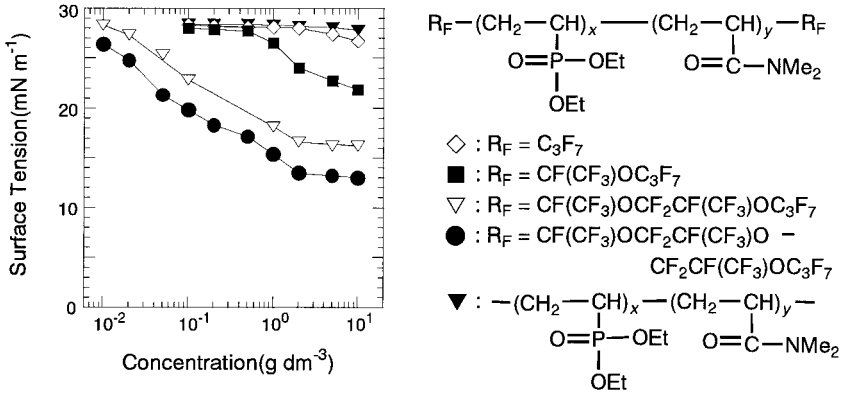


Figure 6 Surface tension of *m*-xylene of R_F–(DEVP)$_x$–(DMAA)$_y$–R_F at 30°C.

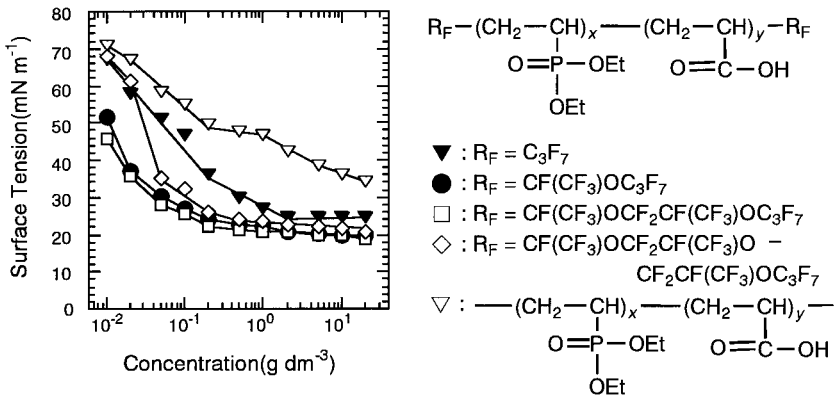


Figure 7 Surface tension of aqueous solutions of R_F–$(DEVP)_x$–$(ACA)_y$–R_F at 30°C.

form only condensed films, which means that the fluoroalkyl groups are almost perpendicular to the water surface and close-packed to each other. This finding suggests that longer fluoroalkyl oligomers are not likely to be parallel to the water surface owing to the steric hindrance of longer fluoroalkyl groups.

Application of Fluoroalkyl End-capped Oligomers to Steel and PMMA Surfaces

It is very interesting to evaluate the adhesive properties of fluoroalkyl end-capped PME and MPE oligomers to metal, since these fluorinated oligomers possess pendant phosphoric acid groups. In fact, these new fluorinated oligomers were tested for stainless-steel surface activity as a new type of phosphorus-containing fluorinated surface-active substances.

Contact angles for dodecane on stainless steel treated with these oligomers are shown in Table VI. Contact angles for dodecane on the treated stainless steel were found to increase significantly compared with those of the corresponding nonfluorinated oligomers and nontreated stainless steel, indicating that the oligomers having longer perfluorooxaalkyl chains possess a higher oil-repellent property.

Similarly, fluoroalkyl end-capped DEVP oligomers are strongly expected to become surface-active to the organic materials such as poly(methyl methacryalte) (PMMA), because these DEVP oligomers possess a good solubility in common organic solvents. Thus, we measured the contact angles for dodecane on the PMMA treated with these oligomers, and the results are shown in Table VII.

As shown in Table VII, significantly large values (23°–62°) of the contact angles of dodecane were observed on the PMMA treated with fluoroalkyl end-capped DEVP oligomers, especially longer fluoroalkylated oligomers, compared to that (0°) of nontreated PMMA. This finding should result from the strong action of fluoroalkyl

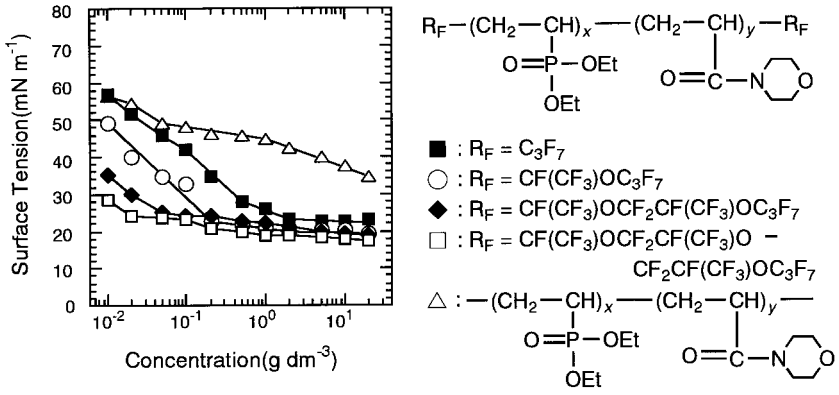
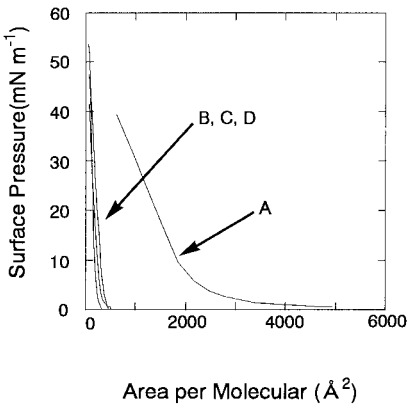


Figure 8 Surface tension of aqueous solutions of R_F–$(DEVP)_x$–$(ACMO)_y$–R_F at 30°C.



$R_F-(CH_2-CH)_n-R_F$
$O=P-OEt$
OEt

A : $R_F = C_3F_7$ ($\overline{Mn}$=2300)

B : $R_F = CF(CF_3)OC_3F_7$ ($\overline{Mn}$=1200)

C : $R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ ($\overline{Mn}$=2400)

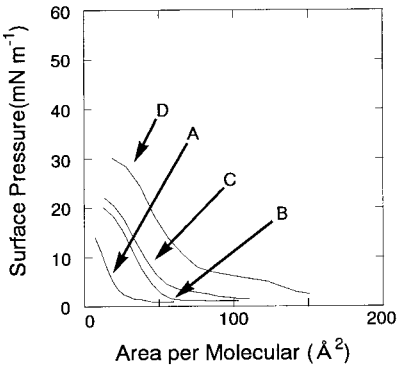
D : $R_F = CF(CF_3)OCF_2CF(CF_3)O - CF_2CF(CF_3)OC_3F_7$ ($\overline{Mn}$=1200)

Figure 9 π-*A* isotherm of fluoroalkylated end-capped DEVP homoligomers.

groups that exhibit an oleophobic property when arranged more regularly above the surface. In conclusion, it was clarified that our present fluoroalkyl end-capped oligomers containing phosphorus segments are applicable to new polymeric fluorinated surface-active substances containing phosphorus atoms.

Hitherto, it was well known that polyanionic compounds, such as dextran sulfate, heparin, pentosan polysulfate, and their derivatives, were shown to be highly potent and selective inhibitors of human immunodeficiency virus type 1(HIV-1) replication *in vitro*.[14] However, a clinical trial with dextran sulfate failed to exhibit a therapeutic effect on AIDS (the acquired immunodeficiency syndrome) patients owing to its low oral bioavailability and rapid degradation *in vivo*.[15] Therefore, it is strongly desirable to explore novel polymeric inhibitors with high stability, potent antiviral activity, and low toxicity. In this respect, we have demonstrated that a series of fluoroalkyl end-capped acrylic acid homo- and cooligomers inhibit HIV-1 *in vitro*,[6a,7a] although it has been already reported that poly(acrylic acid) does not exhibit appreciable activity against HIV-1.[16] From the viewpoint of the development of the attractive anti-HIV-1 agents with high stability, it is very interesting to study the anti-HIV-1 activity of novel fluoroalkyl end-capped oligomers containing pendant phosphoric acid groups, because there have been few reports so far on the approach of polymeric phosphorus derivatives as polymeric inhibitors of HIV-1. In fact, such fluoroalkyl end-capped oligomers were evaluated for activity against HIV-1 replication in MT-4 cells, and the results are shown in Table VIII.

As shown in Table VIII, a series of fluoroalkyl end-capped homo- and cooligomers containing pendant phosphoric acid groups have proved to inhibit HIV-1 replication in cell cultures. The 50% effective concentration (EC_{50}) of these oligomers was 4.0–35 μg mL^{-1} in MT-4 cells, whereas they are not toxic at concentrations up to 100 μg mL^{-1}. On the other hand, the corresponding nonfluori-



$R_F-(CH_2-CH)_x-(CH_2-CH)_y-R_F$
$O=P-OEt$ $O=C-OH$
OEt

A : $R_F = C_3F_7$ ($\overline{Mn}$=800)

B : $R_F = CF(CF_3)OC_3F_7$ ($\overline{Mn}$=1500)

C : $R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ ($\overline{Mn}$=1600)

D : $R_F = CF(CF_3)OCF_2CF(CF_3)O - CF_2CF(CF_3)OC_3F_7$ ($\overline{Mn}$=2200)

Figure 10 π-*A* isotherm of fluoroalkylated end-capped DEVP-ACA cooligomers.

Table VI Contact Angles of Dodecane on Stainless Steel Treated with Fluoroalkylated End-capped PEM and MPE Oligomers

No.	Oligomer	Contact Angle (Degree) Dodecane
	R_F–$(PEM)_n$–R_F	
1	$R_F = C_3F_7$	28
2	$= CF(CF_3)OC_3F_7$	31
3	$= CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	32
	R_F–$(MPE)_n$–R_F	
4	$R_F = C_3F_7$	17
5	$= CF(CF_3)OC_3F_7$	30
6	$= CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	40
	—$(PEM)_n$—	0
	—$(MPE)_n$—	0
	Nontreated stainless steel	0

Table VII Contact Angles of Dodecane Treated with PMMA Films Containing Fluoroalkylated End-capped DEVP Homo- and Cooligomers

No.	Oligomer	Contact Angle (Degree) Dodecane
	R_F–$(DEVP)_n$–R_F	
18	C_3F_7	33
19	$CF(CF_3)OC_3F_7$	34
20	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	33
21	$CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	42
	R_F–$(DEVP)_x$–$(ACA)_y$–R_F	
22	C_3F_7	23
23	$CF(CF_3)OC_3F_7$	54
24	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	60
25	$CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	62
	R_F–$(DEVP)_x$–$(DMAA)_y$–R_F	
26	C_3F_7	32
27	$CF(CF_3)OC_3F_7$	40
28	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	42
29	$CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	48
	R_F–$(DEVP)_x$–$(ACMO)_y$–R_F	
30	C_3F_7	23
31	$CF(CF_3)OC_3F_7$	27
32	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	38
33	$CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	41
	Nontreated	0

Concentration of oligomer is 2% (m/m).

Table VIII Inhibitory Effect of Fluoroalkylated PEM and MPE Oligomers on the Replication of HIV-1 in MT-4 Cells

Oligomer	EC_{50}[a] (μg/mL)	CC_{50}[b] (μg/mL)
R_F–$(PEM)_n$–R_F		
$R_F = C_3F_7$	9.3	>100
$= CF(CF_3)OC_3F_7$	7.7	>100
$= CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	12	>100
R_F–$(MPE)_n$–R_F		
$R_F = C_3F_7$	4.0	>100
$= CF(CF_3)OC_3F_7$	35	>100
R_F–$(PEM)_x$–$(ACMO)_y$–R_F		
$R_F = CF(CF_3)OC_3F_7$	23	>100
$= CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	16	>100
—$(PEM)_n$—	1.6	43
—$(MPE)_n$—	1.6	43

[a] Fifty percent effective concentration, based on the inhibition of HIV-1-induced cytopathicity in MT-4 cells.

[b] Fifty percent cytotoxic concentration, based on the reduction of viability of mock-infected MT-4 cells.

nated PEM and MPE oligomers were toxic to the host cells.

In conclusion, it was demonstrated that fluoroalkanoyl peroxide is a convenient tool for the preparation of various fluoroalkyl end-capped oligomers containing phosphorus segments. In fact, we succeeded in preparing fluoroalkyl end-capped oligomers containing pendant phosphoric acid groups, phosphonic acid oligomers, and phosphonate oligomers under very mild conditions by the use of fluoroalkanoyl peroxide as a key intermediate. Of particular interest, these fluoroalkylated oligomers containing phosphorus segments were clarified to become new attractive functional materials possessing not only unique properties imparted by fluorine and phosphorus but also anti-HIV-activity.

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