Synthesis and Properties of Polymers Based on Oligo(hexafluoropropene oxide) Containing Methacrylates and Copolymers with Methyl Methacrylate

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ABSTRACT: Three series of methacrylate homopolymers with oligo(hexafluoropropene oxide), $(HFPO)_n$, side groups and copolymers based on methyl methacrylate were prepared by free radical polymerization. Each series consisted of a polymethacrylate backbone with substituted HFPO side chains of different length ranging from the corresponding tri- and tetramers to a pentamer. In case of the $(HFPO)_3MA$ copolymers, glass transition temperatures decreased linearly with increasing $(HFPO)_3MA$ content over the entire composition range. In contrast, two different regimes were distinguished for $(HFPO)_5MA$-containing copolymers, and also for the $(HFPO)_4MA$ homopolymer two T_g's were discerned. At low HFPO content the glass transition temperatures decreased with increasing $(HFPO)_5MA$ substitution. Above 50 mol % two glass transitions were observed, indicating microphase separation. Copolymers with only 10 mol % of $(HFPO)_nMA$ exhibited a low surface energy as is typical for highly fluorinated polymers. Dispersion force surface energies were determined by the Good−Girifalco−Fowkes−Young method and resulted in a minimum value of 11 ± 1 mN/m.

Introduction

Per- and semifluorinated materials are widely used because of their low surface energy, chemical inertness, thermal stability, and low friction coefficient.[1] Applications enclose low dielectric constant polymers in electronic industry,[2] friction modifiers in lubrication oils,[3] antifouling coatings,[4] optical fiber claddings,[5−7] and membranes.[8]

Perfluoroalkylalkanes represent an example where the combination of a perfluorinated alkyl and a hydrocarbon segment results in a pronounced amphiphilicity and surface activity.[9−13] Recently, also polymeric amphiphiles have been encountered in the literature.[14−23]

The surface properties of semifluorinated polymers depend on the coverage of the surface by fluorocarbon chains and also on the degree of ordering of these chains. It has been shown that self-assembled monolayers of fluorocarbon chain molecules, in which the surface is formed by close-packed trifluoromethyl groups, possess the lowest surface energy attainable.[24] Similarly, macromolecules with pendent perfluoroalkyl groups which are oriented to the surface can form highly ordered ultralow energy surfaces, provided the side chains are long enough to crystallize above room temperature. Examples are polystyrene modified with perfluorooctyl side groups and poly(methyl methacrylate) with fluorinated side chains larger than perfluorobutyl.[25−27] Monolayers of polymers with fluorinated side chains oriented to the surface can be prepared by the Langmuir−Blodgett technique.[28]

While side chain ordering can be favorable in order to decrease the surface energy, it also can inhibit the formation of low energy surfaces and can result in pronounced instability of thin films, causing dewetting.[26] Furthermore surface crystallization is generally unfavorable for low friction properties.

Regarding these points, it is supposed to be of advantage to replace the perfluoroalkyl groups by perfluoropolyether (PFPE) segments. In particular, hexafluoropropene oxide oligomers and polymers are unable to crystallize. Crystallization is suppressed (i) because of the improved flexibility of the backbone as a result of the ether linkages and (ii) because of the different stereoisomeric combinations of the propene oxide units.[29] Although it must be noted that slow clouding of liquid poly(HFPO) samples has been observed, eventually indicating some phase segregation.[30,31]

Melt surface tension studies of poly(hexafluoropropene oxide) and Cahn−Hilliard density gradient theory suggest that the CF_3 side groups are oriented to the surface.[32] The same conclusion was drawn based upon ion/surface collision experiments in a mass spectrometer[33] and based on XPS measurements of a poly(HFPO) liquid.[34]

PFPEs exhibit excellent thermal stability.[35] The fluorine atoms in α-position to an ether oxygen greatly increase the stability of the ether linkage. The behavior of the oxygen atom is altered from hydrophilic to nonhydrophilic as a result of the changing electronic configuration of the oxygen.[36]

PFPEs are used as lubricants for magnetic recording media,[37] in aerospace applications,[38,39] as emulsifiers for water and oil applications and in supercritical carbon dioxide,[40−44] as additives for oil and water repellent coatings[45−49] and in polyurethane networks,[50] as novel elastomers,[30,51−53] and as fluorinated resins for low solvent paints.[54]

In our research we focused on methacrylate homopolymers with HFPO side groups of varying length. Also, three series of copolymers with methyl methacrylate were prepared.

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Experimental Part

Materials. Methyl perfluoro-2,5-dimethyl-3,6-dioxanonanoate, methyl perfluoro-2,5,8-trimethyl-3,6,9-trioxadodecanoate and methyl perfluoro-2,5,8,11-tetramethyl-3,6,9,12-tetraoxapentadecanoate (all ≥97%; PCR) were used as received. Dichloromethane (technical quality) was distilled on a rotary evaporator and subsequently distilled over phosphorus pentoxide. Tetrahydrofuran (THF, technical quality) was dried over potassium/benzophenone. Methanol (technical quality) was distilled before use. 1,3-Bis(trifluoromethyl)benzene (99%; Aldrich) and 1,1,2-trichlorotrifluoroethane (Freon-113, Merck, p.a.) were used as received. Methacrylic anhydride (94%; Aldrich) was distilled in vacuo. Methyl methacrylate (99%; MMA, Aldrich) was stirred over calcium hydride overnight at 40 °C and distilled at reduced pressure. 2,2′-Azobisisobutyronitrile (Aldrich) was recrystallized from methanol. 4-(Dimethylamino)pyridine (99+%; Aldrich) and lithium aluminum hydride (Merck) were used as received.

Hexafluoropropene Oxide *n*-Mer Alcohol [$(HFPO)_nOH$] (a Typical Example Described). A 500 mL three-necked flask fitted with a condenser, an addition funnel and a nitrogen inlet was charged with a solution of 5.0 g (132 mmol) of $LiAlH_4$ in 200 mL of THF. To this solution was added dropwise 60 g (118 mmol) of methyl perfluoro-2,5-dimethyl-3,6-dioxanonanoate in 100 mL of THF. After addition was complete, the solution was refluxed overnight. Excess $LiAlH_4$ was deactivated by the careful addition of diluted hydrochloric acid. Then dichloromethane, mixed with some 1,1,2-trichlorotrifluoroethane, was added, and the organic phase was washed two times with diluted hydrochloric acid. The collected aqueous phases were extracted with dichloromethane/1,1,2-trichlorotrifluoroethane. The combined organic phases were dried and concentrated. The remaining liquid was distilled under reduced pressure (67 °C/26 mbar) to give 49.6 g of a colorless liquid.

***1H*,*1H*-Perfluoro-2,5-dimethyl-3,6-dioxanonan-1-ol [$(HFPO)_3OH$]:** clear colorless liquid; yield 87%; purity >99% (GC/MS). ^1H NMR ($CDCl_3$/1,1,2-trichlorotrifluoroethane): 4.12 (d, 2H, $-CH_2-$, $^3J_{H-F} = 12.3$ Hz), variable (2−5) (bs, 1H, $-OH$). ^{13}C NMR ($CDCl_3$/1,1,2-trichlorotrifluoroethane): 61.2 (d, $-CH_2-$, $^2J_{C-F} = 29.3$ Hz), 100−125 (fluorinated carbon region). ^{19}F NMR ($CDCl_3$/1,1,2-trichlorotrifluoroethane): −79.4 to −82.8 (m, 13F, all $-CF_2-O-$ and $-CF_3$ signals), −130.0 (m, 2F, $CF_3-CF_2-CF_2-$), −136.4 (m, 1F, $-C(CF_3)F-CH_2-$), −145.0 (m, 1F, $-C(CF_3)FCF_2-$). GC/MS (CI, CH_4): $m/z = 483$ (MH^+).

***1H*,*1H*-Perfluoro-2,5,8-trimethyl-3,6,9-trioxadodecan-1-ol [$(HFPO)_4OH$]:** clear colorless liquid; bp 55−56 °C/0.9 mbar; yield 96%; purity >98% (GC/MS). ^1H NMR ($CDCl_3$/1,1,2-trichlorotrifluoroethane): 4.14 (d, 2H, $-CH_2-$, $^3J_{H-F} = 11.3$ Hz), variable (2−5) (bs, 1H, $-OH$). ^{13}C NMR ($CDCl_3$/1,1,2-trichlorotrifluoroethane): 61.1 (d, $-CH_2-$, $^2J_{C-F} = 29.0$ Hz), 99−125 (fluorinated carbon region). ^{19}F NMR ($CDCl_3$/1,1,2-trichlorotrifluoroethane): −78.0 to −83.1 (m, 18F, all $-CF_2-O-$ and $-CF_3$ signals), −130.3 (m, 2F, $CF_3-CF_2-CF_2-$), −136.0 (m, 1F, $-C(CF_3)F-CH_2-$), −145.5 (m, 2F, $-C(CF_3)FCF_2-$). GC/MS (CI, CH_4): $m/z = 649$ (MH^+).

***1H*,*1H*-Perfluoro-2,5,8,11-tetramethyl-3,6,9,12-tetraoxapentadecan-1-ol [$(HFPO)_5OH$]:** clear colorless liquid; bp 54−55 °C/0.06 mbar; yield 97%; purity >98% (GC/MS). ^1H NMR ($CDCl_3$/1,1,2-trichlorotrifluoroethane): 4.16 (d, 2H, $-CH_2-$, $^3J_{H-F} = 12.6$ Hz), variable (2−5) (bs, 1H, $-OH$). ^{13}C NMR ($CDCl_3$/1,1,2-trichlorotrifluoroethane): 61.2 (d, $-CH_2-$, $^2J_{C-F} = 28.9$ Hz), 97−125 (fluorinated carbon region). ^{19}F NMR ($CDCl_3$/1,1,2-trichlorotrifluoroethane): −78.2 to −82.7 (m, 23F, all $-CF_2-O-$ and $-CF_3$ signals), −129.8 (m, 2F, $CF_3-CF_2-CF_2-$), −136.0 (m, 1F, $-C(CF_3)F-CH_2-$), −144.6 (m, 3F, $-C(CF_3)FCF_2-$). GC/MS (CI, CH_4): $m/z = 815$ (MH^+).

Hexafluoropropene Oxide *n*-Mer Methacrylate [$(HFPO)_nMA$] (a Typical Example Described). A 250 mL three-necked flask was charged with 20 g (31 mmol) of $(HFPO)_4OH$, and a mixture of 75 mL of dichloromethane and 25 mL of 1,1,2-trichlorotrifluoroethane was used as solvent. Then 0.46 g (3.6 mmol) of 4-(dimethylamino)pyridine was added followed by 4.6 g (30 mmol) of methacrylic anhydride. After several minutes 4 mL (30 mmol) of triethylamine was added, and the mixture was stirred at 30 °C overnight. The mixture was subsequently washed with water, diluted hydrochloric acid, a 4 wt % solution of sodium hydrogen carbonate and water. The combined aqueous layers were extracted with dichloromethane/1,1,2-trichlorotrifluoroethane. This organic layer was combined with the extracted reaction mixture, dried, and filtered, and the solvent was removed on a rotary evaporator to give 18,8 g of a lightly yellow liquid.

***1H*,*1H*-Perfluoro-2,5-dimethyl-3,6-dioxanonan-1-yl Methacrylate [$(HFPO)_3MA$]:** clear lightly yellow liquid; yield 95%; purity >99% (GC/MS). ^1H NMR: 1.94 (s, 3H, $-CH_3$), 4.68 (d, 2H, $-CH_2-$, $^3J_{H-F} = 10.6$ Hz), 5.68 (s, 1H, vinylic proton trans to carbonyl), 6.17 (s, 1H, vinylic proton cis to carbonyl). ^{13}C NMR: 17.8 ($-CH_3$), 60.0 (d, $-CH_2-$, $^2J_{C-F} = 32.1$ Hz), 100−125 (fluorinated carbon region), 127,7 ($CH_2{=}$), 134.5 (${=}C{<}$), 165.2 ($C{=}O$). ^{19}F NMR: −80.5 to −83.6 (m, 13F, all $-CF_2-O-$ and $-CF_3$ signals), −130.2 (m, 2F, $CF_3-CF_2-CF_2-$), −134.6 (d, 1F, $-C(CF_3)F-CH_2-$), −145.5 (m, 1F, $-C(CF_3)F-CF_2-$). GC/MS (CI, CH_4): $m/z = 551$ (MH^+).

***1H*,*1H*-Perfluoro-2,5,8-trimethyl-3,6,9-trioxadodec-1-yl Methacrylate [$(HFPO)_4MA$]:** clear lightly yellow liquid; yield 85%; purity >99% (GC/MS). ^1H NMR: 1.93 (s, 3H, $-CH_3$), 4.67 (d, 2H, $-CH_2-$, $^3J_{H-F} = 10.7$ Hz), 5.65 (s, 1H, vinylic proton trans to carbonyl), 6.16 (s, 1H, vinylic proton cis to carbonyl). ^{13}C NMR: 17.8 ($-CH_3$), 59.9 (d, $-CH_2-$, $^2J_{C-F} = 31.7$ Hz), 100−125 (fluorinated carbon region), 127.8 ($CH_2{=}$), 134.7 (${=}C{<}$), 165.4 ($C{=}O$). ^{19}F NMR: −80.2 to −83.7 (m, 18F, all $-CF_2-O-$ and $-CF_3$ signals), −130.3 (m, 2F, $CF_3-CF_2-CF_2-$), −134.2 (m, 1F, $-C(CF_3)F-CH_2-$), −145.5 (m, 2F, $-C(CF_3)F-CF_2-$). GC/MS (CI, CH_4): $m/z = 717$ (MH^+).

***1H*,*1H*-Perfluoro-2,5,8,11-tetramethyl-3,6,9,12-tetraoxapentadec-1-yl Methacrylate [$(HFPO)_5MA$]:** clear lightly yellow liquid; yield 90%; purity 99% (GC/MS). ^1H NMR: 1.92 (s, 3H, $-CH_3$), 4.67 (d, 2H, $-CH_2-$, $^3J_{H-F} = 10.6$ Hz), 5.65 (s, 1H, vinylic proton trans to carbonyl), 6.15 (s, 1H, vinylic proton cis to carbonyl). ^{13}C NMR: 17.9 ($-CH_3$), 60.0 (d, $-CH_2-$, $^2J_{C-F} = 31.9$ Hz), 100−125 (fluorinated carbon region), 127.8 ($CH_2{=}$), 134.7 (${=}C{<}$), 165.4 ($C{=}O$). ^{19}F NMR: −80.7 to −83.8 (m, 23F, all $-CF_2-O-$ and $-CF_3$ signals), −130.4 (m, 2F, $CF_3-CF_2-CF_2-$), −133.8 (m, 1F, $-C(CF_3)F-CH_2-$), −145.4 (m, 3F, $-C(CF_3)F-CF_2-$). GC/MS (CI, CH_4): $m/z = 883$ (MH^+).

Polymerizations were carried out in 15 mL glass bottles with Teflon-coated screw caps. A 1 mol % sample of 2,2′-azobisisobutyronitrile (AIBN) was weighed into the bottle followed by the monomers at the desired ratios. Then a small amount of 1,3-bis(trifluoromethyl)benzene was added as solvent, and the solution was degassed with nitrogen for ca. 10 min. The bottles were sealed with Parafilm and the homogeneous solutions were allowed to stir for 60 h at 60 °C. The polymer was precipitated in distilled methanol, filtered, and dried under vacuo at 40 °C to constant weight. Homopolymers and MMA/$(HFPO)_5MA$ copolymers up to 50 mol % $(HFPO)_5MA$ were clear, viscous materials. All other polymers were white powders.

Gel permeation chromatography (GPC) was performed in toluene at room temperature. The setup consisted of a Waters 590 programmable HPLC pump, a HP Ti−Series 1050 autosampler, a set of Waters μ-Styragel columns (10^5, 10^4, 10^3, and 10^6 Å), and as detectors a viscometer detector H502B (Viscotheck) and a Waters 410 differential refractometer. The flow rate was 1.5 mL/min. The solvent was degassed by means of a Knauer degasser. Narrow polydispersity poly(styrene) standards (PSS) were used for calibration. GPC-WIN version 2.54 software from PSS was used for the evaluation.

Thermogravimetric analysis was conducted by means of a TG System from Perkin-Elmer. Platinum was used as the reference material. Measurements were performed under a nitrogen atmosphere. Decomposition temperatures, T_{dec}, were taken at the temperature at which the onset for a change in dm/dT arose.

Differential scanning calorimetry (DSC) was performed with a DSC-7 differential scanning calorimeter from Perkin-Elmer. Pans (50 μL) with type 0.15 caps (Perkin-Elmer) were chosen for the samples. The runs were processed with TAS-7 software. The low-temperature measurements were calibrated with cyclopentane, cyclohexane, water, gallium, and indium. Unless stated otherwise, samples were heated at a rate of 20 K/min.

Viscosity measurements were performed with a capillary viscometer (Schott, Type 531.03) in an automated setup (Schott AVS 350). Toluene was used as solvent. The temperature was maintained at 30 °C.

^{1}H, ^{13}C, and ^{19}F NMR analyses in $CDCl_3$ (99.8%, Deutero GmbH.; stored over 4 Å molecular sieves) were recorded on a Bruker AC 200 spectrometer at 200, 50, and 188 MHz respectively. Chemical shifts of the ^{1}H and ^{13}C spectra were related to the $CHCl_3$ signal at 7.24 and 77.0 ppm, respectively. Chemical shifts of the ^{19}F spectra were related to the $CFCl_3$ signal at 0 ppm.

GC/MS was performed on a Finnigan MAT SSQ 7000 mass spectrometer coupled to a Varian 3400 gas chromatograph. The GC-column (DB-5 MS from J & W Scientific), had a length of 30 m, an internal diameter of 0.25 mm and a film thickness of 0.25 μm. Helium was used as carrier gas at a flow rate of ca. 1 mL/min.

Contact angles were measured (i) by means of the Wilhelmy plate technique and (ii) by using the sessile drop method. A KSV Sigma 70 system was used for the Wilhelmy plate measurements. Advancing and receding contact angles were obtained by dipping polymer coated glass plates in *n*-hexadecane. Sessile drop measurements were carried out with a G40 (Krüss GmbH) contact angle measuring instrument using separate 500 μL syringes for each wetting liquid. A homologous series of *n*-alkanes (octane, decane, dodecane, and hexadecane, all p.a. quality) was used as the wetting liquid. The temperature was maintained at 20 ± 0.1 °C by means of a Ministate (Huber) digital thermostat.

Samples were prepared by the following procedure: Small glass plates measuring 24 × 24 mm^2 (Wilhelmy plate: 18 × 18 mm^2) were washed with a mixture of sulfuric acid and hydrogen peroxide and rinsed several times with bidistilled water. Then the plates were washed with distilled acetone and dried at room temperature. The cleaned glass plates were coated with 1 wt % polymer solutions in chloroform or 1,1,2-trichlorotrifluoroethane by using a spin casting apparatus at 3000 rpm for 10 s.

Results and Discussion

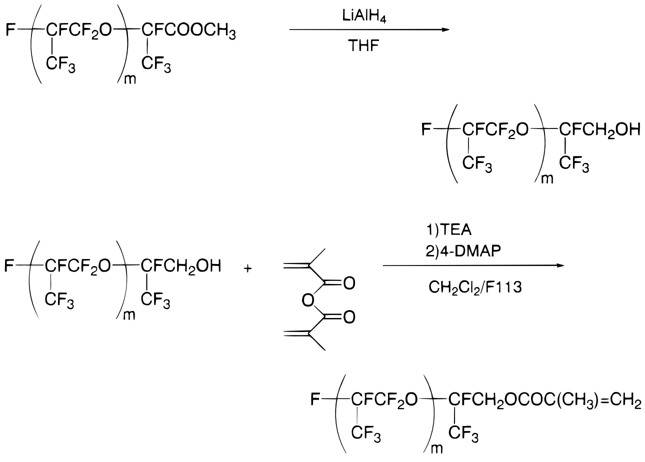
Synthesis. Hexafluoropropene oxide *n*-mer alcohols, $(HFPO)_nOH$, were prepared by reduction of the respective methyl esters, according to a modified literature procedure.[55] In a second step, the alcohols were esterified with methacrylic anhydride (Scheme 1). All products were obtained in good yields and high purities.

Three series of hexafluoropropene oxide (HFPO) containing methacrylates were polymerized radically. Each series consisted of a HFPO homopolymer and several statistical copolymers with methyl methacrylate (MMA). The length of the HFPO units was varied from trimer ($m = 2$) and tetramer ($m = 3$) to pentamer ($m = 4$) (Scheme 2).

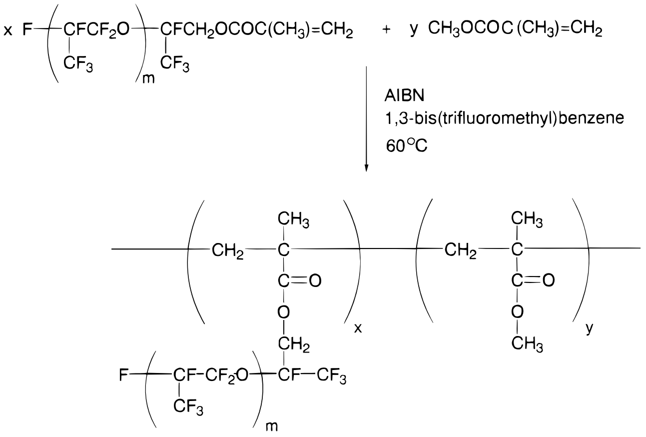
Characterization of the polymers regarding molecular weight and composition is displayed in Table 1.

The composition data were determined by ^{1}H NMR. The values were in agreement with the composition of the feed. Regarding the homogeneity of the samples and the similar chemical reactivity of semifluorinated methacrylate monomers,[56] it can be assumed that both monomers are randomly distributed along the polymer chain.

Scheme 1



Scheme 2



The solubility of the (co)polymers was qualitatively determined. Toluene was chosen as a good solvent for PMMA, and 1,1,2-trichlorotrifluoroethane as a good solvent for $P[(HFPO)_nMA]$. It is apparent that the solubility depended strongly on the composition of the copolymers and on the length of the HFPO oligomers. The trimer, $(HFPO)_3MA$, containing copolymer was soluble in 1,1,2-trichlorotrifluoroethane when the $(HFPO)_3MA$ content was 20 mol %. At the same composition the copolymer was also soluble in toluene and chloroform. Tetra- and pentameric HFPO copolymers of the same composition were insoluble in toluene, while they could still be dissolved in 1,1,2-trichlorotrifluoroethane even when as much as 90% MMA was present.

For copolymers which were soluble in toluene, i.e., copolymers with a high MMA content, the molecular weights were determined by GPC using both relative calibration according to narrow polystyrene standards and universal calibration by means of a viscometer detector connected parallely to a refractive increment detector. From Table 1 it can be seen that molecular weights according to the relative calibration decreased with increasing HFPO content, while the universal calibration yielded similar molecular weights independent of the amount of HFPO present. Only for the copolymers with the highest MMA content did the molecular weights obtained by the relative calibration and the universal calibration method converge. This might be ascribed to the extent to which the coil conformation collapsed due to the poorly soluble fluorinated units in the copolymers and the correspondingly

Table 1. Molecular Weight, Composition, and Yields for the Prepared $(HFPO)_nMA$ Homopolymers and $(HFPO)_nMA/MMA$ Copolymers

polymer	M_n[a] (kg/mol)	M_n[b] (kg/mol)	M_w/M_n[a]	M_w/M_n[b]	MMA content[c] (mol %)	yield (%)
P[$(HFPO)_3$-MA]	*d*	*d*	*d*	*d*		89
P(MMA-*co*-$(HFPO)_3$-MA)-50/50	*d*	*d*	*d*	*d*	46	92
P(MMA-*co*-$(HFPO)_3$-MA)-80/20	19		1.78	*e*	78	94
P(MMA-*co*-$(HFPO)_3$-MA)-90/10	43	131	2.26	2.03	90	96
P(MMA-*co*-$(HFPO)_3$-MA)-95/5	74	101	1.83	2.06	95	95
P(MMA-*co*-$(HFPO)_3$-MA)-99/1	91	106	2.04	2.19	*f*	96
P[$(HFPO)_4$-MA]	*d*	*d*	*d*	*d*		90
P(MMA-*co*-$(HFPO)_4$-MA)-50/50	*d*	*d*	*d*	*d*	46	94
P(MMA-*co*-$(HFPO)_4$-MA)-80/20	5.5	*e*	1.50	*e*	81	94
P(MMA-*co*-$(HFPO)_4$-MA)-90/10	69	165	2.08	2.01	90	95
P(MMA-*co*-$(HFPO)_4$-MA)-95/5	108	175	2.07	2.12	*f*	96
P(MMA-*co*-$(HFPO)_4$-MA)-99/1	127	153	2.12	2.53	*f*	96
P[$(HFPO)_5$-MA]	*d*	*d*	*d*	*d*		90
P(MMA-*co*-$(HFPO)_5$-MA)-26/74						95
P(MMA-*co*-$(HFPO)_5$-MA)-50/50	*d*	*d*	*d*	*d*	*g*	90
P(MMA-*co*-$(HFPO)_5$-MA)-72/28	*d*	*d*	*d*	*d*	*g*	90
P(MMA-*co*-$(HFPO)_5$-MA)-80/20	*d*	*d*	*d*	*d*	*g*	91
P(MMA-*co*-$(HFPO)_5$-MA)-90/10	28	*e*	1.90	*e*	89	91
P(MMA-*co*-$(HFPO)_5$-MA)-95/5	41	114	2.66	1.57	*f*	87
P(MMA-*co*-$(HFPO)_5$-MA)-99/1	78	118	1.72	1.95	*f*	93

[a] GPC measurements in toluene with polystyrene standards. [b] GPC measurements in toluene with universal calibration. [c] As determined from ^1H NMR. [d] Could not be determined due to insolubility of polymer. [e] The small visco-signal did not allow quantitative analysis. [f] HFPO signal too small to calculate ratio. [g] No quantitative determination of ratio possible because of low solubility of the polymer in $CDCl_3$.

Table 2. Properties of $(HFPO)_nMA$ Homopolymers and $(HFPO)_nMA/MMA$ Copolymers[a]

polymer	$[\eta]$ (mL/g) capillary viscometer	$[\eta]$ (mL/g) GPC	T_g (°C)	T_{dec} (°C)
P[$(HFPO)_3$MA]			−8	237
P(MMA-*co*-$(HFPO)_3$MA)-50/50			47	242
P(MMA-*co*-$(HFPO)_3$MA)-80/20			78	233
P(MMA-*co*-$(HFPO)_3$MA)-90/10		24	105	248
P(MMA-*co*-$(HFPO)_3$MA)-95/5		44	102	234
P(MMA-*co*-$(HFPO)_3$MA)-99/1	67	65	110	238
P[$(HFPO)_4$MA]			−34/58	251
P(MMA-*co*-$(HFPO)_4$MA)-50/50			39	249
P(MMA-*co*-$(HFPO)_4$MA)-80/20			77	246
P(MMA-*co*-$(HFPO)_4$MA)-90/10	28	36	101	246
P(MMA-*co*-$(HFPO)_4$MA)-95/5	57	63	109	245
P(MMA-*co*-$(HFPO)_4$MA)-99/1	68	73	121	249
P[$(HFPO)_5$MA]			−47/74	236
P(MMA-*co*-$(HFPO)_5$MA)-26/74			−43/96	245
P(MMA-*co*-$(HFPO)_5$MA)-50/50			−42/40	237
P(MMA-*co*-$(HFPO)_5$MA)-72/28			54	239
P(MMA-*co*-$(HFPO)_5$MA)-80/20			72	237
P(MMA-*co*-$(HFPO)_5$MA)-90/10			96	236
P(MMA-*co*-$(HFPO)_5$MA)-95/5	31	38	111	237
P(MMA-*co*-$(HFPO)_5$MA)-99/1	41	42	115	246

[a] Limiting viscosity numbers were measured in toluene at 30 °C. Glass transition temperatures were obtained from the second heating run at 20 K/min. Decomposition temperatures were determined under nitrogen atmosphere.

lowered hydrodynamic volume. Universal calibration is based on the relationship between the limiting viscosity number, $[\eta]$, and both hydrodynamic volume, V_h, and the molecular weight, M, as expressed in the Einstein−Simha equation (eq 1),

$$[\eta] = \psi N_A V_h/M$$

$$V_h \propto [\eta]M \qquad (1)$$

where ψ is the Simha factor for shape correction, which is 2.5 for ideal spheres, and N_A is the Avogadro number.

Limiting viscosity numbers were determined using a capillary viscometer as well as a viscometer detector in the GPC setup (Table 2). Both values agreed rather well and showed the same distinct decrease with increasing HFPO content. On the basis of the observation that both the hydrodynamic volume and the limiting viscosity decreased with increasing HFPO content, by using eq 1 it can be reasoned that the molecular weight is hardly affected by the fraction of HFPO-substituted monomer.

Thermal Properties. Thermal properties of the synthesized alcohols, monomers, and polymers were studied by thermogravimetric analysis and differential scanning calorimetry.

For the methyl esters, the alcohols, and the methacrylate monomers, a glass transition was found (Table 3). The glass transition temperature, T_g, increased monotonically with increasing HFPO chain length. However, different T_g's were found depending on the type of end group, i.e., ester, alcohol, or methacrylate.

Figures 1 −3 display the glass transition temperatures of the tri-, tetra-, and pentamer-substituted polymers as a function of composition (see also Table 2). The copolymers containing pendent trimer HFPO chains show a linear decrease in T_g with increasing HFPO content as expected for statistical copolymers. However, for the series with the HFPO tetramer side chains two T_g's were found for the homopolymer. Two glass transitions were also observed for the polymers with the pentamer side groups, provided the fraction of $(HFPO)_5$-substituted monomer was higher than 50 mol %. For low contents of $(HFPO)_5$MA the glass transition temperature decreased steeply as a function of the composition. Increasing the amount of $(HFPO)_5$MA resulted in a T_g at a rather constant level around −40 °C. At the same time a second glass transition was recorded at higher temperatures. This discontinuity may be regarded as an indication for segregation of a HFPO-rich and a polymethacrylate-rich microphase. All polymers which gave two glass transitions were clear and homogeneous as expected for microphase-separated materials.

Table 3. Glass Transition Temperatures of Low Molecular Weight HFPO Compounds

compound	T_g (°C)
$(HFPO)_3CO_2CH_3$	−118
$(HFPO)_4CO_2CH_3$	−107
$(HFPO)_5CO_2CH_3$	−101
$(HFPO)_3OH$	−94
$(HFPO)_4OH$	−88
$(HFPO)_5OH$	−84
$(HFPO)_3MA$	−110
$(HFPO)_4MA$	−98
$(HFPO)_5MA$	−93

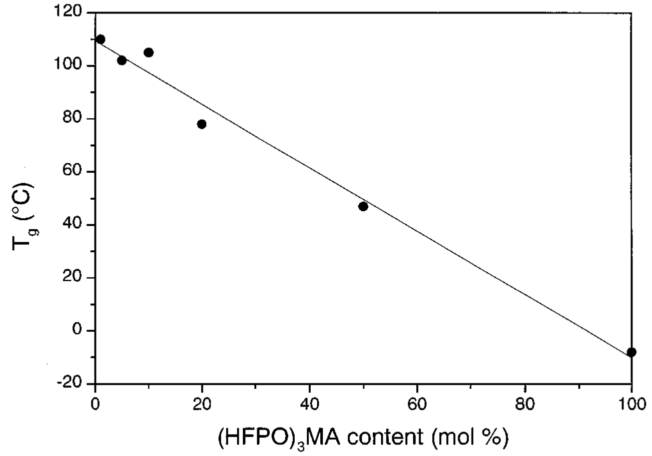


Figure 1. Glass transition temperatures as a function of the $(HFPO)_3MA$ content. T_g's were determined at the second heating run at a rate of 20 K/min.

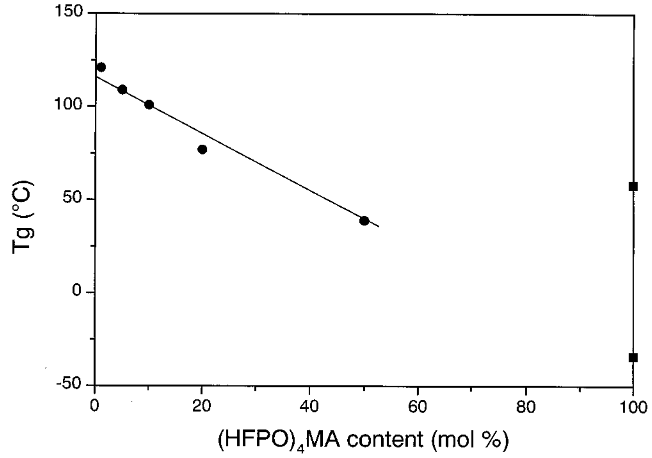


Figure 2. Glass transition temperatures as a function of the $(HFPO)_4MA$ content. T_g's were determined at the second heating run at a rate of 20 K/min. Split T_g's are indicated by (■); single T_g's are depicted by (●).

Corresponding DSC traces comparing P(MMA-*co*-$(HFPO)_5MA$)-72/28 in the one-phase region (A) with P(MMA-*co*-$(HFPO)_5MA$)- 50/50 in the microphase separated state (B) are illustrated in Figure 4. As the heat capacities of the first glass transition were decreasing with decreasing $(HFPO)_5MA$ content the low-temperature region was assigned to the HFPO-rich phase.

For all samples neither DSC traces nor thermooptical investigations between crossed polarizers rendered any evidence for crystallization effects.

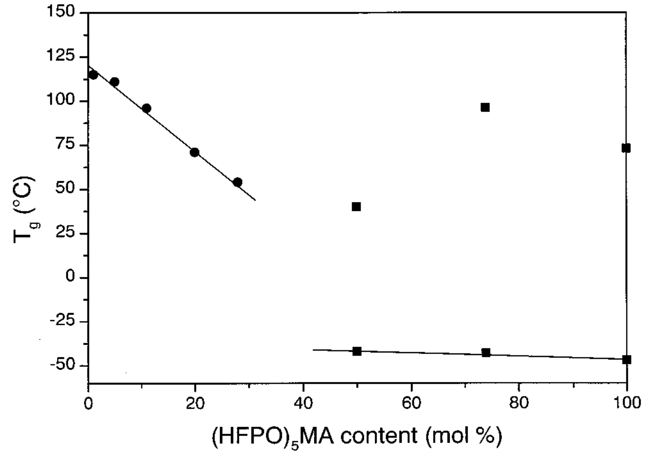


Figure 3. Glass transition temperatures as a function of the $(HFPO)_5MA$ content. T_g's were determined at the second heating run at a rate of 20 K/min. Split T_g's are indicated by (■); single T_g's are depicted by (●).

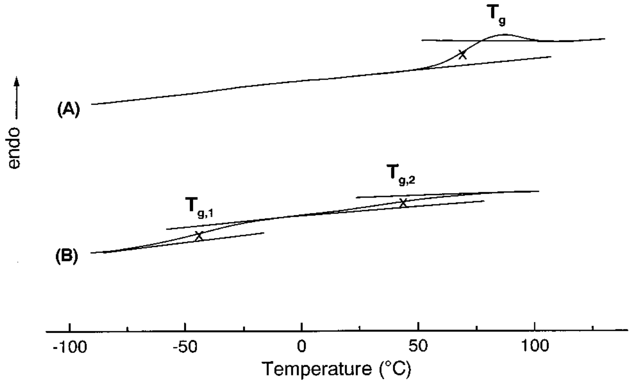


Figure 4. DSC traces for P(MMA-*co*-$(HFPO)_5MA$)-72/28 (A) and P(MMA-*co*-$(HFPO)_5MA$)-50/50 (B) at the second heating run at a rate of 20 K/min.

Thermogravimetric analyses showed that in all cases degradation takes place in two steps. Apparently, the ester linkages in the side groups break up first, followed by an overall decomposition of the backbone in the second step. Decomposition temperatures are given in Table 2.

Surface Behavior. A series of *n*-alkanes was used as wetting liquid to determine the contact angle, θ, by means of the sessile drop method. The Good−Girifalco−Fowkes−Young (GGFY) equation[57,58] was applied for the calculation of the dispersion force surface energy, γ_s^D[59,60]

$$\cos(\theta) = -1 + 2(\gamma_s^D)^{1/2}(\gamma_L)^{-1/2} \qquad (2)$$

in which γ_L is the surface tension of the wetting liquid. This approach is valid for normal alkanes, as the polar contribution to the energy of adhesion is absent and only the dispersion interactions are taken into account. When $\cos(\theta)$ is plotted as a function of $(\gamma_L)^{-1/2}$ the dispersion force surface energy can be obtained from regression analysis.

Contact angles for *n*-hexadecane as wetting liquid as a function of HFPO content are given in Figure 5. Initially, a marked increase in θ was observed, as a function of the amount of incorporated $(HFPO)_nMA$, up to about 10% $(HFPO)_nMA$. After this point θ leveled off and remained high for all compositions.

Correspondingly, γ_s^D approached equally low values at high $(HFPO)_nMA$ content for all three HFPO series. The lowest γ_s^D value measured was 11 ± 1 mN/m for the tri- and tetramer homopolymers. At low (HF-

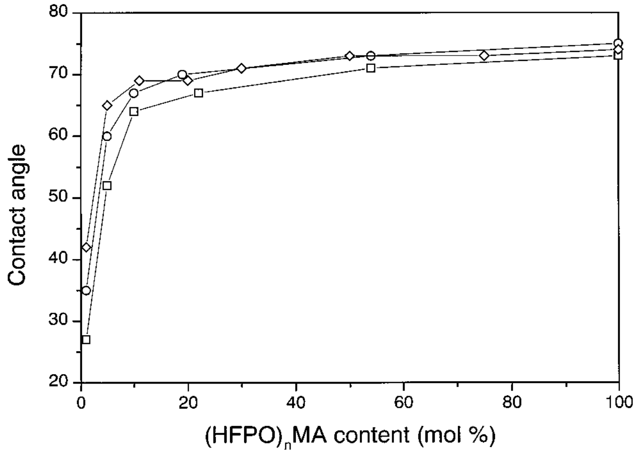


Figure 5. Contact angle of a drop of n-hexadecane on a coated plate with (HFPO)$_3$MA (□), (HFPO)$_4$MA (○), and (HFPO)$_5$MA (◇) (co)polymers as a function of (HFPO)$_n$MA content at 20 °C. Coated glass plates were prepared at room temperature.

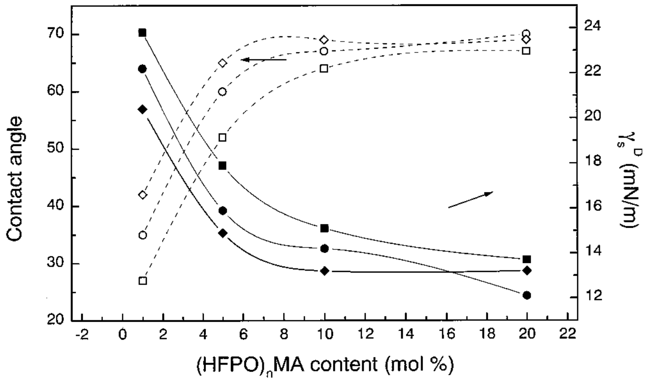


Figure 6. Contact angle (···) and dispersion force surface energy (—) vs (HFPO)$_n$MA content. (HFPO)$_3$MA (□, ■), (HFPO)$_4$MA (○, ●) and (HFPO)$_5$MA (◇, ◆) (co)polymers as a function of (HFPO)$_n$MA content at 20 °C. Coated glass plates were prepared at room temperature.

PO)$_n$MA content, the copolymer with the longer substituents displayed a significantly larger lipophobicity (see Figure 6). The (HFPO)$_3$MA series showed the highest γ_s^D value (24 ± 1 mN/m). This might be explained by the higher volume fraction of the fluoroether segments and a correspondingly better surface coverage of the longer HFPO segments. Chart 1 depicts a schematical representation for the surface coverage with HFPO units, where the CF$_3$ groups are directed toward the surface.[32] Such an explanation accounts for the structure of the HFPO side chains involving flexibility and incapability of crystallizing and thereby allows an optimum orientation at the surface.

The effect of annealing on the contact angles of (HFPO)$_4$MA containing (co)polymers was studied by the Wilhelmy plate method. The corresponding advancing and receding contact angles are listed in Table 4. Hysteresis, expressed by $\Delta\theta = \theta_a - \theta_r$, decreased with decreasing (HFPO)$_4$MA content. At higher (HFPO)$_4$MA content, the effect of annealing was negligible which was expected because of high flexibility of the HFPO units at ambient temperatures.

Hydrophobicity of the HFPO surfaces was tested by contact angle measurements against water. Sessile drop contact angles of (HFPO)$_4$MA (co)polymers, which were measured on as prepared films (θ_1) and after annealing at 110 °C (θ_2), are depicted in Table 5. The high values of about 110° manifest strong hydrophobicity of the films. Also in this case, the annealing procedure did not affect the contact angles that indicate the equilibrium surface structure of the films.

Chart 1

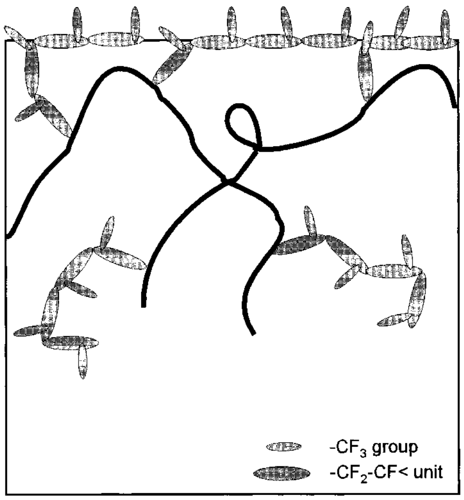


Table 4. Advancing, θ_a, and Receding, θ_r, Contact Angles (deg) of (HFPO)$_4$MA/MMA (Co)polymers As Measured by Means of the Wilhelmy Plate Technique[a]

sample (mol % HFPO)	remarks	θ_a	θ_r	$\Delta\theta$
100	used as prepared	80 ± 1	53 ± 1	27 ± 2
50	used as prepared	72 ± 2	48 ± 1	24 ± 3
20	used as prepared	69 ± 1	52 ± 2	17 ± 3
5	used as prepared	57 ± 1	45 ± 1	12 ± 2
100	18 h, 110 °C	80 ± 1	53 ± 1	27 ± 1
50	18 h, 110 °C	71 ± 1	52 ± 1	19 ± 2
20	18 h, 110 °C	70 ± 1	60 ± 1	10 ± 1
5	18 h, 110 °C	63 ±1	55 ± 1	8 ± 1

[a] *n*-Hexadecane was used as wetting liquid (surface tension was determined to be 27.42 mN/m). T = 20.2 °C.

Table 5. Water Contact Angles of (HFPO)$_4$MA/MMA (Co)polymers on As Prepared Films (θ_1) and after Annealing for 18 h at 110 °C (θ_2)

sample (mol % HFPO)	$\theta_1^{a,b}$	$\theta_2^{a,b}$
100	*c*	113
50	112 ± 1	112 ± 1
20	114 ± 1	113 ± 1
5	106 ± 1	108 ± 1

[a] The angles were determined by the sessile drop method at T = 20 °C. [b] Doubly distilled water was used as a wetting liquid. [c] No stable drop could be obtained because of continuous spreading and decrease of the contact angle.

In contrast to linear fluorinated alkyl side chains, which show high contact angles only after annealing,[61] HFPO-containing polymers possess already a high degree of hydro- and lipophobicity without an additional temperature treatment.

Conclusions

HFPO-containing polymers were shown to give low energy surfaces. Similar to polymers with linear perfluoroalkyl side chains, a surface layer of fluorinated groups provided the lipophobic character. Copolymers consisting of HFPO methacrylate and methyl methacrylate exhibited already a low surface energy with only 10 mol % of (HFPO)$_n$MA. At low HFPO substitution, copolymers reduced the surface energy more efficiently with increasing length of the side groups, i.e., trimer < tetramer < pentamer. This was explained by an improved surface coverage with HFPO chains for the longer HFPO oligomers. The lowest dispersion force surface energy obtained was 11 ± 1 mN/m.

Due to their low glass transition temperatures HFPO polymers displayed a low surface energy without annealing. Annealing resulted in a slight reduction of the surface energy only for copolymers with low HFPO content. At higher contents the mobility of the HFPO side chains is high enough to achieve an optimal surface coverage at ambient temperature.

In the case of the tetrameric and pentameric HFPO side chains, glass transition temperatures did not decrease linearly with increasing (HFPO)$_n$MA content over the entire composition range. Microphase separation could be observed depending on the fraction of HFPO monomer. In the case of the tetramer, two glass transitions were observed for the homopolymer. The pentamer containing polymers showed two different T_g's when 50 mol % or more of (HFPO)$_5$MA was incorporated in the copolymer.

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