Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis and Mesoscopic Organization of Perfluoroalkyl-Alkylene Methacrylate Monomers

Jens Höpken [a] , Sabine Faulstich [a] & Martin Möller [a]

[a] Department of Chemical Technology, University of Twente, P.O. Box 217, 7500 AE, Enschede, The Netherlands

Version of record first published: 24 Sep 2006.

To cite this article: Jens Höpken , Sabine Faulstich & Martin Möller (1992): Synthesis and Mesoscopic Organization of Perfluoroalkyl-Alkylene Methacrylate Monomers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 210:1, 59-73

To link to this article: http://dx.doi.org/10.1080/10587259208030757

Mol. Cryst. Liq. Cryst., 1992, Vol. 210, pp. 59–73
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Synthesis and Mesoscopic Organization of Perfluoroalkyl-Alkylene Methacrylate Monomers

JENS HÖPKEN, SABINE FAULSTICH and MARTIN MÖLLER†

Department of Chemical Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

(Received May 27, 1991)

Alcohols with perfluorinated segments, $F(CF_2)_n$—$(CH_2)_m$—OH; n = 8, 10, 12; m = 4, 6, 10; have been converted into methacrylates by a dicyclohexylcarbodiimide activated esterification reaction. The resulting methacrylates show two disordering transitions prior to isotropization. Polarization optical microscopy indicates the occurrence of smectic liquid crystal phases. Organic solutions of the amphiphilic methacrylates showed a strong decrease in the surface tension at low concentrations. Peculiar surface activity had already been observed for the compound with the shortest fluorocarbon segment. Needle shaped crystallites of the semifluorinated compounds are formed when hydrocarbon solutions of methacrylates with a perfluorododecyl substituent are cooled. The crystals can form a fine mesh network which encloses the solvent in the cavities. The size of the needle crystals and the internal dimensions of the network depend strongly on the crystallization conditions.

INTRODUCTION

Molecules in which a fluorocarbon and a hydrocarbon moiety are linked together possess a strong amphiphilic character. By analogy with the behavior of normal surfactants, the incompatibility of the segments causes aggregation of the fluorocarbon-hydrocarbon diblock molecules in the bulk and in non-aqueous solution.

Reports on the structural characterization of *n*-alkanes with perfluorinated segments with up to 12 carbons have demonstrated that crystallization occurs with the molecules in lamellar structures.[1–3] However, the detailed packing mode of the individual molecules within the lamellae is still unknown. As the cross-section of the fluorocarbon segment exceeds by far that of the hydrocarbon segment, a regular arrangement in a densely packed crystal cannot be modelled straightforwardly. In a recent article,[4] we presented transmission electron microscopic evidence for a cylindrical 24 nm superstructure in $F(CF_2)_{12}$-$(CH_2)_{20}H$, in the form of crystallites which can be explained by concentric double layered lamellae.

In calorimetric studies of *n*-alkanes with perfluorinated segments one or, in most

† To whom correspondence should be sent.

cases, even two phase transitions were observed before isotropization,[1,3,5,6] indicating a stepwise conversion from the ordered crystal to the isotropic melt. Solid state ^{13}C-NMR experiments[6,7] showed that in the mesomorphic state the hydrocarbon segments are highly mobile and conformationally disordered while the regularity in the packing of the fluorocarbon segments is retained.

Crystallization of sequentially perfluorinated compounds from dilute solution in organic solvents resulted in the formation of extremely long thin crystals which become interlocked in disarray and build up a three dimensional network, which can enclose large amounts of solvent in the cavities.[6]

Phase diagrams of semifluorinated alkane/hydrocarbon solvent systems, as well as semifluorinated alkane/fluorocarbon solvent systems indicated association in solution. Light scattering experiments in dilute solution confirmed association in hydrocarbon solvents.[6] "Inverse micelles" were observed using fluorocarbon solvents.[8]

The results mentioned above represent different examples or aspects of a peculiar tendency of the semifluorinated compounds for self-organization within defined supermolecular structures in the bulk, as well as in non-aqueous solution.

The monodisperse structure of the low molecular weight diblock molecules allows organization into very defined and regular structures, whereby the strong incompatibility of the two segments accounts for a sharp separation of the microdomains. In contrast, polydispersity is an inherent feature of block copolymers, and the generally much weaker incompatibility of the constituent polymer blocks causes less perfect separation at the domain boundaries.[9] Thus, the supermolecular organization too, i.e., the formation of ordered microdomain morphologies, cannot be as precise and regular as it is the case with low molecular weight compounds.

Association or micelle formation of defined low molecular weight perfluoroalkyl-alkylene compounds appears to be of fundamental interest, because the driving force for dissolution and association in non-aqueous, non-polar solvents is basically of an enthalpic nature,[8] while micelle formation of surfactants in aqueous solution is largely entropy driven.[10] However, if one regards true micelle formation as a liquid-liquid segregation, it must be noted that it cannot be distinguished yet whether the formation of soluble multimers is not partly due to crystallization effects. The observed formation of needle crystals with extreme aspect ratios might be an indication that rather stable, ultra-small crystallites are formed, which are soluble as a whole.

Large linear fluorocarbon segments favour association or aggregation, but also crystallization,[6,8,11] and dissolved associates are only observed within a small concentration-temperature window. Low temperatures and high concentrations result in macroscopic crystallization. Elevated temperatures favour molecular dissolution. Perfluoroalkyl-alkanes with linear fluorocarbon and hydrocarbon segments, $F(CF_2)_m$—$(CH_2)_nH$, which have been studied so far,[6,8] crystallize easily, and are not particularly suitable for the investigation of the association behavior. The macroscopic solubility is increased in the case of fluorocarbon-hydrocarbon molecules which carry an allyl ether functionality at the end of the hydrocarbon segment.[11] For these compounds, a pronounced surface activity was observed in organic solution, indicating preferential adsorption of the solute in the solution/air

interface. Furthermore, the temperature range of the thermotropic liquid crystalline phase was also considerably increased in comparison to the nonfunctionalized diblock molecules.[6,11]

In summary, it can be seen that introduction of functional groups represents a means to alter the phase and dissolution behavior of perfluoroalkyl-alkylene systems. A consequent further step is the substitution into the molecules of polymerizable groups. Polymerization can help to stabilize organized structures, and stringing up small molecules to a polymer chain results in a geometric pre-ordering. In the case of conventional surfactants, polymerization increases the stability of micelles, vesicles,[12] and lyotropic, as well as thermotropic mesophases.[13,14] Consequently, the synthesis of polymers with sequentially perfluorinated side chains of variable lengths is a tempting pathway towards new materials with peculiar properties.

In the present article, we report the synthesis of methacrylate monomers with long perfluorocarbon substituents by using a mild esterification reaction. The thermotropic liquid crystalline behavior and the self-organization of the amphiphilic monomers in non-aqueous solution is investigated. Polymerization of these methacrylate monomers in the isotropic, as well as in preordered phases will be reported in a forthcoming article.[15]

EXPERIMENTAL PART

Materials

Perfluorodecyl and perfluorododecyl iodide (Hoechst AG, 98%) were recrystallized from toluene. 2,2'-Azoisobutyronitrile (Merck) was crystallized from methanol at temperatures below 40°C. Hex-5-en-1-ol (Merck, > 90%) was carefully fractionated by distillation and obtained > 99% pure. All other reagents were used without further purification. Sample purity was checked by gas chromatography.

Perfluoroalkyl-alkylene methacrylates, $F(CF_2)_n(CH_2)_m$—OOC—$C(CH_3)$=CH_2 [n = 8, 10, 12; m = 2, 4, 6, 10]. Perfluoroalkyl-alkylene methacrylates were prepared by two different methods. First, 1-perfluoroalkyl-ω-alkanols were reacted with methacrylic acid in an azeotropic esterification. As an example, 1-perfluorododecyl-ω-hexanol (20 mmol), methacrylic acid (120 mmol), *p*-toluenesulfonic acid (0.2 g, 1 mmol), 2,6-di-t-butyl-*p*-cresol (0.2 g, 0.5 mmol) and 1,1,2-trichlorotrifluoroethane ($ClCF_2 \cdot CCl_2F$, 250 ml) were placed under a N_2-atmosphere in an apparatus for azeotropic extraction. Limited solubility of the semifluorinated alcohol, even at the boiling temperature of the solvent, prevented formation of a homogeneous solution. On circulation, the solvent was passed through molecular sieves to remove the water liberated during the reaction. After 4 days of reaction, the 1,1,2-trichlorotrifluoroethane was evaporated off, and the remaining solid material suspended in ether (50 ml), and washed with dilute aqueous sodium hydrogencarbonate solution (250 ml). The solid was filtered off and dried. Characterization by ^{1}H-NMR and gas chromatography revealed that conversion was not complete. The product still contained unreacted alcohol. The methacrylates with

a perfluorodecyl or a perfluorododecyl segment were sublimed under high vacuum at 50°C to achieve purification. Perfluorooctyl-ethylene methacrylate was purified by distillation under reduced pressure. Purities were checked by gas chromatography.

$F(CF_2)_{10}$—$(CH_2)_4$—OOC—$C(CH_3)$=CH_2: yield = 54%, purity = 89%, ^{1}H-NMR [$CDCl_3$, δ_{TMS} in ppm]: 1.60–1.80 ppm [t, —CF_2—CH_2—$C\underline{H}_2$—$C\underline{H}_2$—, 4 protons]; 1.95 ppm [s, —$C(C\underline{H}_3)$=CH_2, 3 protons]; 2.0–2.3 ppm [tt, —CF_2—$C\underline{H}_2$—CH_2—, 2 protons]; 4.20 ppm [t, —CH_2—$C\underline{H}_2$—O—, 2 protons]; 5.58 ppm and 6.12 ppm [2 s, —$C(CH_3)$=$C\underline{H}_2$, 1 proton].

$F(CF_2)_{12}$—$(CH_2)_4$—OOC—$C(CH_3)$=CH_2: yield = 61%, purity = 93%, ^{1}H-NMR [$CDCl_3$, δ_{TMS} in ppm]: 1.65–1.90 ppm [t, —CF_2—CH_2—$C\underline{H}_2$-$C\underline{H}_2$—, 4 protons]; 1.95 ppm [s, —$C(C\underline{H}_3)$=CH_2, 3 protons]; 2.1–2.3 ppm [tt, —CF_2—$C\underline{H}_2$—CH_2—, 2 protons]; 4.20 ppm [t, —CH_2—$C\underline{H}_2$—O—, 2 protons]; 5.55 ppm and 6.12 ppm [2 s, —$C(CH_3)$=$C\underline{H}_2$, 1 proton].

$F(CF_2)_{12}$—$(CH_2)_{10}$—OOC—$C(CH_3)$=CH_2: yield = 74%, purity = 90%, ^{1}H-NMR [$CDCl_3$/Freon 113, δ_{TMS} in ppm]: 1.2–1.45 ppm [broad s, —CF_2—CH_2—CH_2—$(C\underline{H}_2)_2$—CH_2—CH_2—, 4 protons]; 1.6–1.8 ppm [broad s, —CF_2—CH_2—$C\underline{H}_2$—$(CH_2)_2$—$C\underline{H}_2$—CH_2—, 4 protons]; 1.94 ppm [s, —$C(C\underline{H}_3)$=CH_2, 3 protons]; 2.0–2.2 ppm [tt, —CF_2—$C\underline{H}_2$—CH_2—, 2 protons]; 4.14 ppm [t, —CH_2—$C\underline{H}_2$—O—, 2 protons]; 5.55 ppm and 6.11 ppm [s, —$C(CH_3)$=$C\underline{H}_2$, 1 proton].

Better results were obtained by a modified catalyzed esterification procedure reported by Hassner.[16] As an example, 1-perfluoroalkyl-ω-alkanol (50 mmol), methacrylic acid (51 mmol), dicyclohexylcarbodiimide (DCC) (51 mmol) and dimethylaminopyridine (DMAP) (5 mmol) were added to 1,1,2-trifluorotrichloroethane (Freon 113) (200 ml). Upon mixing of the reactants, an exothermic reaction was noted, whereon the mixture was stirred at room temperature for a minimal 5 h. After the reaction was complete, the N,N-dicyclohexylurea was removed by filtration and the filtrate was washed with water, 5% aqueous acetic acid, and again with water. Evaporation of the solvent gave the crude products which were contaminated with any unreacted DCC. No unconverted alcohol was found in the product mixture. The methacrylate with a perfluorooctyl segment was purified by distillation. The methacrylates with longer fluorocarbon segments were crystallized from acetone. Sample purities were checked by gas chromatography.

$F(CF_2)_8$—$(CH_2)_2$—OOC—$C(CH_3)$=CH_2: yield = 60%, purity = 99.1%, b.p.: 51°C (0.3 torr), ^{1}H-NMR [$CDCl_3$, δ_{TMS} in ppm]: 1.95 ppm [s, —$C(C\underline{H}_3)$=CH_2, 3 protons]; 2.53 ppm [tt, —CF_2—$C\underline{H}_2$—CH_2—, 2 protons]; 4.45 ppm [t, —CF_2—CH_2—$C\underline{H}_2$—O—, 2 protons]; 5.53 ppm and 6.15 ppm [s, —$C(CH_3)$=$C\underline{H}_2$, 1 proton].

$F(CF_2)_{10}$—$(CH_2)_6$—OOC—$C(CH_3)$=CH_2: yield = 73%, purity = 98.7%, ^{1}H-NMR [$CDCl_3$, δ_{TMS} in ppm]: 1.45 ppm [broad s, —CF_2—CH_2—CH_2—$(C\underline{H}_2)_2$—CH_2—CH_2—, 4 protons]; 1.6–1.8 ppm [broad s, —CF_2—CH_2—$C\underline{H}_2$—$(CH_2)_2$—$C\underline{H}_2$—CH_2—, 4 protons]; 1.95 ppm [s, —$C(C\underline{H}_3)$=CH_2, 3 protons]; 2.0–2.3 ppm [tt, —CF_2—$C\underline{H}_2$—CH_2—, 2 protons]; 4.16 ppm [t, —CH_2—$C\underline{H}_2$—O—, 2 protons]; 5.57 ppm and 6.05 ppm [s, —$C(CH_3)$=$C\underline{H}_2$, 1 Proton].

$F(CF_2)_{12}$—$(CH_2)_6$—OOC—$C(CH_3)$=CH_2: yield = 65%, purity = 98.8%, ^{1}H-

NMR [$CDCl_3$/Freon 113, δ_{TMS} in ppm]: 1.45 ppm [broad s, —CF_2—CH_2—CH_2—$(CH_2)_2$—CH_2—CH_2—, 4 protons]; 1.6–1.8 ppm [broad s, —CF_2—CH_2—CH_2—$(CH_2)_2$—CH_2—CH_2—, 4 protons]; 1.94 ppm [s, —$C(CH_3)$=CH_2, 3 protons]; 2.0–2.3 ppm [tt, —CF_2—CH_2—CH_2—, 2 protons]; 4.16 ppm [t, —CH_2—CH_2—O—, 2 protons]; 5.57 ppm and 6.12 ppm [s, —$C(CH_3)$=CH_2, 1 proton].

Gas chromatography was done using a Varian 3700 equipped with a two meter 22.5% QF-1 column, using helium as carrier gas at temperatures between 130°C and 280°C.

1H-NMR spectra were recorded on a Nicolet 200 MHz spectrometer using $CDCl_3$ and mixtures of $CDCl_3$ and 1,1,2-trichlorotrifluoroethane (Freon 113) as solvents at 25°C; $CHCl_3$ at 7.26 ppm and TMS at 0 ppm acted as internal standards.

Thermal analysis was performed using a Perkin Elmer DSC-7, equipped with a PE-7700 computer and TAS-7 software. Phase transition temperatures were read as the peak temperatures of the heating endotherms recorded at a heating rate of 2 K/min with samples of 2–3 mg weight. For the determination of the phase transition enthalpies, samples of about 10 mg were used, and the heats of transition were calculated by integration of the peaks. Phase transition entropies were calculated from the enthalpies assuming thermal equilibrium conditions. Glass transition temperatures, as determined by the point of inflection in the heat capacity step, were extrapolated to heating rate zero.[17] Gallium and indium were used as calibration standards.

Surface tension measurements were performed with a Krüss K12 electronic balance tensiometer, using a platinum Wilhelmy plate with a perimeter of 40.0 mm.

Infra-red spectra were recorded using a Biorad Digilab Division FTS-60 spectrometer equipped with a diffusion reflection cell, a Digilab 3200 computer, and software.

Polarization microscopy was performed with a Leitz Ortholux II Pol BK Microscope, equipped with a Mettler FP82 hot stage and a FP80 central processor. Thin layers of the pure compounds were obtained by melting a small amount of the solid material placed on a microscopic slide and covered with a cover slip. For the observation of gel formation flattened capillaries with an internal height of 0.1 mm or 0.05 mm were dipped into heated solutions of the methacrylates in toluene. After gelation of the solution upon cooling, the capillaries were hermetically closed by fusing both ends in a flame.

RESULTS AND DISCUSSION

a. Synthesis

A detailed description of the preparation of the 1-perfluoroalkyl-ω-alkanols has been given previously.[11] They were prepared in two reaction steps. First, the 1-perfluoroalkyl iodides were reacted with ω-alk-1-enols in a free radical addition

TABLE I

Melting and disordering transition temperatures, and enthalpies and entropies of transition for perfluoroalkyl-alkylene methacrylates

R = —OC(CH$_3$)=CH$_2$	T_{d1}	ΔH_{d1}	ΔS_{d1}	T_{d2}	ΔH_{d2}	ΔS_{d2}	T_m	ΔH_m	ΔS_m
F(CF$_2$)$_{12}$(CH$_2$)$_{10}$—OR				337	5	15	368	21	59
F(CF$_2$)$_{12}$(CH$_2$)$_{14}$—H				363	16	45	366	26	73
F(CF$_2$)$_{12}$(CH$_2$)$_6$—OR	312	12	38	320	1	3	363	22	61
F(CF$_2$)$_{12}$(CH$_2$)$_{10}$—H	207	1	6	342	9	28	365	25	71
F(CF$_2$)$_{12}$(CH$_2$)$_4$—OR	297	10	34	301	0.4	1	360	21	57
F(CF$_2$)$_{12}$(CH$_2$)$_8$—H	192	3	12	329	6	19	361	24	66
F(CF$_2$)$_{10}$(CH$_2$)$_6$—OR	306	14	46	311	1	3	321	15	48
F(CF$_2$)$_{10}$(CH$_2$)$_{10}$—H	317	4	13				337	24	73
F(CF$_2$)$_{10}$(CH$_2$)$_4$—OR	297	10	34	311	0.5	2	319	15	47
F(CF$_2$)$_8$(CH$_2$)$_2$—OR	210	5	25				253	9	34

process to yield 1-perfluoroalkyl-2-iodo-ω-alkanols,[18] which in the second reaction step were reduced to 1-perfluoroalkyl-ω-alkanols by tributyltin hydride.[19]

$$F(CF_2)_n—I + CH_2=CH—(CH_2)_{m-2}—OH$$

$$\xrightarrow{AIBN} F(CF_2)_n—CH_2—CHI—(CH_2)_{m-2}—OH$$

$$F(CF_2)_n—CH_2—CHI—(CH_2)_{m-2}—OH$$

$$\xrightarrow{AIBN,\ Bu_3SnH} F(CF_2)_n—(CH_2)_m—OH$$

The sequentially perfluorinated alcohols were characterized by gas chromatography and ^{1}H-NMR spectroscopy. Purities were better than 97%.

Preparation of the methacrylates was handicapped by the insolubility of the perfluoroalkyl-alcohols in common organic solvents. Solubility studies on perfluoroalkyl-alkanes showed that their dissolution depends strongly on the length of the fluorocarbon segment and increases as the temperature is raised.[6] However, as methacrylates tend to polymerize at higher temperatures, we attempted the azeotropic esterification of methacrylic acid with the semifluorinated alcohols in suspension in trichlorotrifluoroethane (Freon 113), which boils at 48°C forming an azeotropic mixture which contains 1% wt of water.[20] 2,6-Di-*t*-butyl-*p*-cresol was added as a polymerization inhibitor. Even after 4 days the reaction was not complete.

To avoid tedious and time consuming purification, further semifluorinated meth-

acrylates were prepared by the mild esterification method described in the experimental section. The process is catalyzed by a dialkylaminopyridine.[21]

$$CH_2{=}C(CH_3){-}COOH + F(CF_2)_n{-}(CH_2)_m{-}OH + C_6H_{11}{-}N{=}C{=}N{-}C_6H_{11}$$

$$\xrightarrow{DMAP} CH_2{=}C(CH_3){-}COO{-}(CH_2)_m{-}(CF_2)_nF + (C_6H_{11}{-}NH)_2{-}C{=}O$$

Freon 113 was used as the solvent, but the perfluorodecyl and perfluorododecyl substituted alcohols were not completely soluble. Quantitative conversions were obtained after 5 hours. The perfluoroalkyl-alkylene methacrylates had purities better than 98%—see the experimental part. The NMR-assignment for $CH_2{=}C(CH_3){-}COO{-}(CH_2)_6{-}(CF_2)_{12}F$ is given below:

$$\underset{1}{F(CF_2)_{12}}\underset{2}{-CH_2-}\underset{3}{CH_2-}\underset{3}{CH_2-}\underset{2}{CH_2-}\underset{4}{CH_2-}OOC-\underset{5}{C(CH_3)}=\underset{6,7}{CH_2}$$

1	2.0–2.0 ppm	2H, three triplets
2	1.2–1.4 ppm	4H, multiplet
3	1.6–1.8 ppm	4H, broad singlet
4	4.45 ppm	2H, triplet
5	1.95 ppm	3H, singlet
6	5.55 ppm	1H, singlet
7	6.10 ppm	1H, singlet

b. Thermal Analysis (DSC)

The phase behavior of the semifluorinated methacrylates was investigated by differential scanning calorimetry (DSC) and optical polarizing microscopy. Table I summarizes the temperatures, and the enthalpy and entropy changes for the observed phase transitions in direct comparison with those for the corresponding semifluorinated *n*-alkanes. The isotropization temperatures for the fluorocarbon substituted methacrylates do not deviate considerably from the values found for perfluoroalkyl-alkanes[1,6,7] ($F(CF_2)_n{-}(CH_2)_mH$) or the semifluorinated allyl ethers[11] ($F(CF_2)_n{-}(CH_2)_m{-}OCH_2CH{=}CH_2$) of corresponding segmental lengths.

All except one semifluorinated methacrylate undergo two mesomorphic transitions before isotropization. Such behavior was also observed for the semifluorinated allyl ethers and *n*-alkanes. As demonstrated in Table I and Figure 1, considerable transition enthalpies are noted for the first mesomorphic transition T_{d1}, while only small thermal effects were found at the second, upper, transition T_{d2}. Figure 1 also shows that the disordering transition at T_{d1} exhibited considerably stronger undercooling than that observed for the transition at T_{d2} and the isotropization. In the case of $F(CF_2)_8{-}(CH_2)_2{-}OOC{-}CH_3{=}CH_2$, the disordering and the melting peak could not be separated completely.

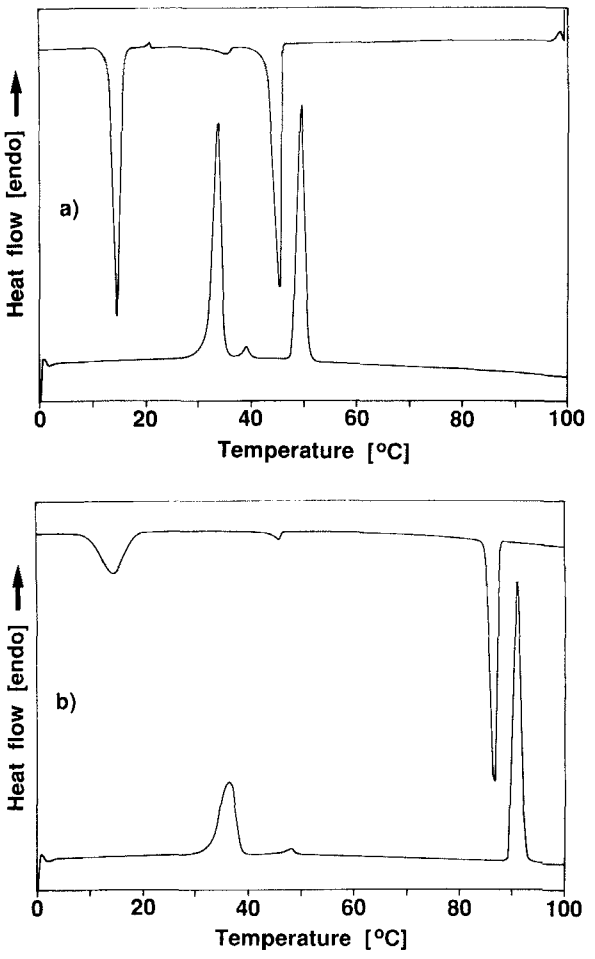

FIGURE 1 DSC heating and cooling traces for *a*) $F(CF_2)_{10}(CH_2)_6$—OOC—$(CH_3)C{=}CH_2$ and *b*) $F(CF_2)_{12}(CH_2)_6$—OOC—$(CH_3)C{=}CH_2$.

Most of the corresponding semifluorinated alcohols $F(CF_2)_n$—$(CH_2)_m$—OH, showed no mesomorphic transitions.[11] The melting points were about 40°C higher than those of the unfunctionalized semifluorinated *n*-alkanes. This might be explained by strong intermolecular interactions in the crystalline state by hydrogen bridges.

Melting temperatures and entropies of the perfluoroalkyl methacrylates depend strongly on the length of the fluorocarbon segment and do not vary much for compounds with different hydrocarbon segments. In contrast, the values found for T_{d1} increase with increasing length of the hydrocarbon segment, but stay essentially constant for compounds with different fluorocarbon segments. This indicates that, at T_{d1}, molecular mobility becomes possible primarily in the hydrocarbon segments. No such correlation can be given for the second disordering transition.

c. Optical Polarizing Microscopy

Optical polarization microscopy yielded further insight into the structure of the mesomorphic phases detected by thermal analysis. In the case of nonfunctionalized, sequentially perfluorinated linear alkanes, $F(CF_2)_n$—$(CH_2)_mH$, cooling of the isotropic melt gave a smectic liquid crystalline phase. As is typical for the smectic B state,[22] a bâtonnet texture was observed with large black homotropic areas, which turned bright when the sample was sheared or tilted.[5-7]

The same texture was also found for allyl ethers with fluorocarbon segments, $F(CF_2)_n$—$(CH_2)_m$—$OCH_2CH{=}CH_2$, in a large temperature range between the upper disordering transition and the isotropization.[11] A lower disordering transition of little entropy was found at temperatures too low for polarization optical observation.

A different phase behavior was observed in the DSC experiments for the perfluoroalkyl-alkylene methacrylates. As shown in Figure 1, a second disordering transition of small entropy was found above the large disordering peak which is common for all fluorocarbon-hydrocarbon diblock systems and which indicates the transition to a smectic liquid crystalline structure. The question arises as to whether two different liquid crystalline phases might be observed for the methacrylates.

Bâtonnets and platelets, which are characteristic for a smectic B phase[22] separated from the isotropic melt upon cooling below the melting point. This texture, shown in Figure 2*a*, was only stable within a temperature range of about 1 K below the isotropization point. Further cooling resulted in the formation of platelet and mosaic textures as shown in Figure 2*b* for $F(CF_2)_{10}$—$(CH_2)_6$—$OCH_2CH{=}CH_2$. Comparison of the textures with those observed for reference liquid crystalline compounds[22] and consideration of the plausibility of the changes regarding the molecular structure suggest the assignment of a smectic G structure to this phase. In both, S_B and S_G phases, the molecules are in a hexagonally or pseudohexagonally close packed arrangement. While in the S_B structure the long axes of the molecules are oriented perpendicular to the smectic layers, in the S_G structure they are tilted at approximately 25°–30°.[22] At the S_B to S_G transition, the individual molecules in the layers do not tilt. Instead, molecules are displaced relative to each other parallel to their long axes leading to an effective tilt of the smectic layers. Confirmation or otherwise of this assignment has to be obtained by X-ray experiments.

Only small changes were observed in the polarizing microscopic texture when the methacrylates were cooled below the upper, weak disordering transition observed by DSC. As shown in Figure 2*c*, the mosaic areas become cross-hatched with a large number of parallel lines. This has been described as characteristic for the transition of a smectic G to a smectic H phase,[22] equivalent to a change from the hexagonally close packed structure to the orthorhombic close packed one. The very small transition entropy observed by DSC supports the idea of a change in the molecular packing without conformational changes.

Upon cooling below the first disordering transition, crystallization is observed as shown in Figure 2*d*.

Summarizing it can be stated, that introduction of the methacrylic functionality into the molecular structure leads to an extension of the temperature range of liquid crystalline phases in comparison to the behavior of nonfunctionalized fluo-

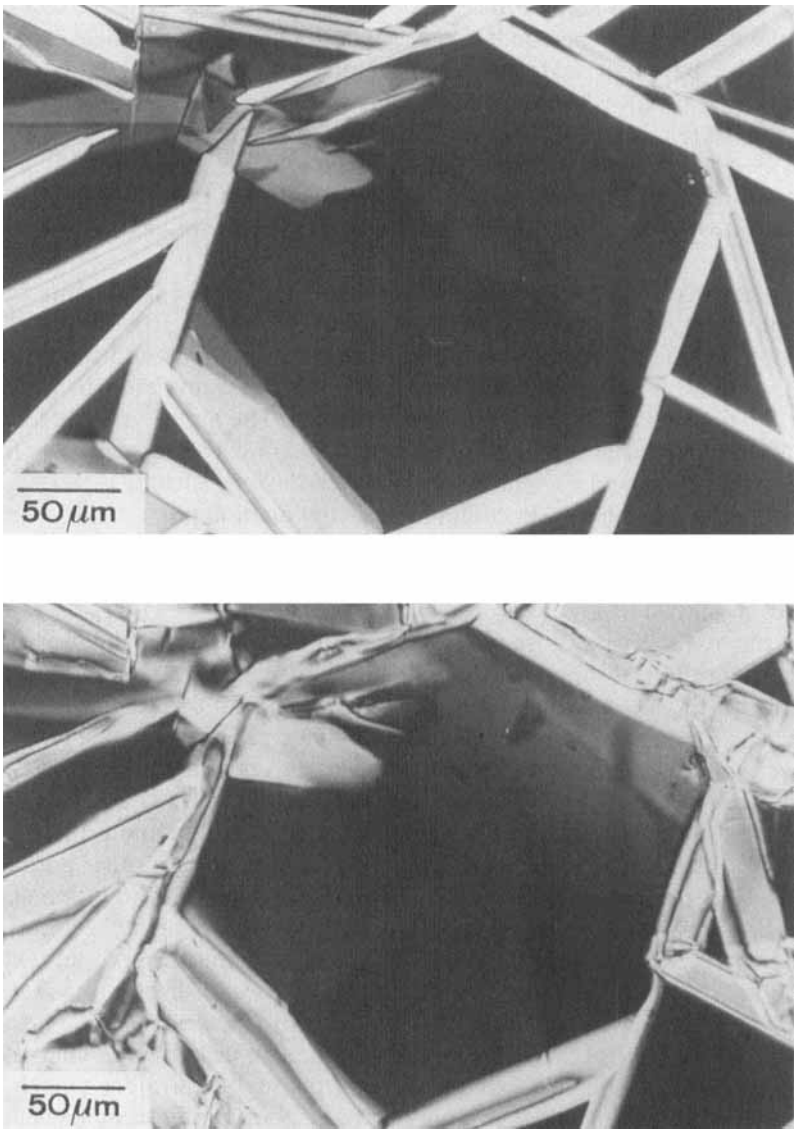

FIGURE 2 Microphotographs showing the birefringent textures of $F(CF_2)_{10}(CH_2)_6$—OOC—(CH_3)-C=CH_2 between crossed polarizers, *a*) 48.4°C; separation of bâtonnets and platelets from the isotropic melt, *b*) 44.4°C; mosaic texture with large homogeneous areas observed between T_{d2} and T_i, *c*) 29.0°C; mosaic texture observed between T_{d1} and T_{d2}, *d*) 20.0°C; crystalline phase observed below T_{d1}. See Color Plate I.

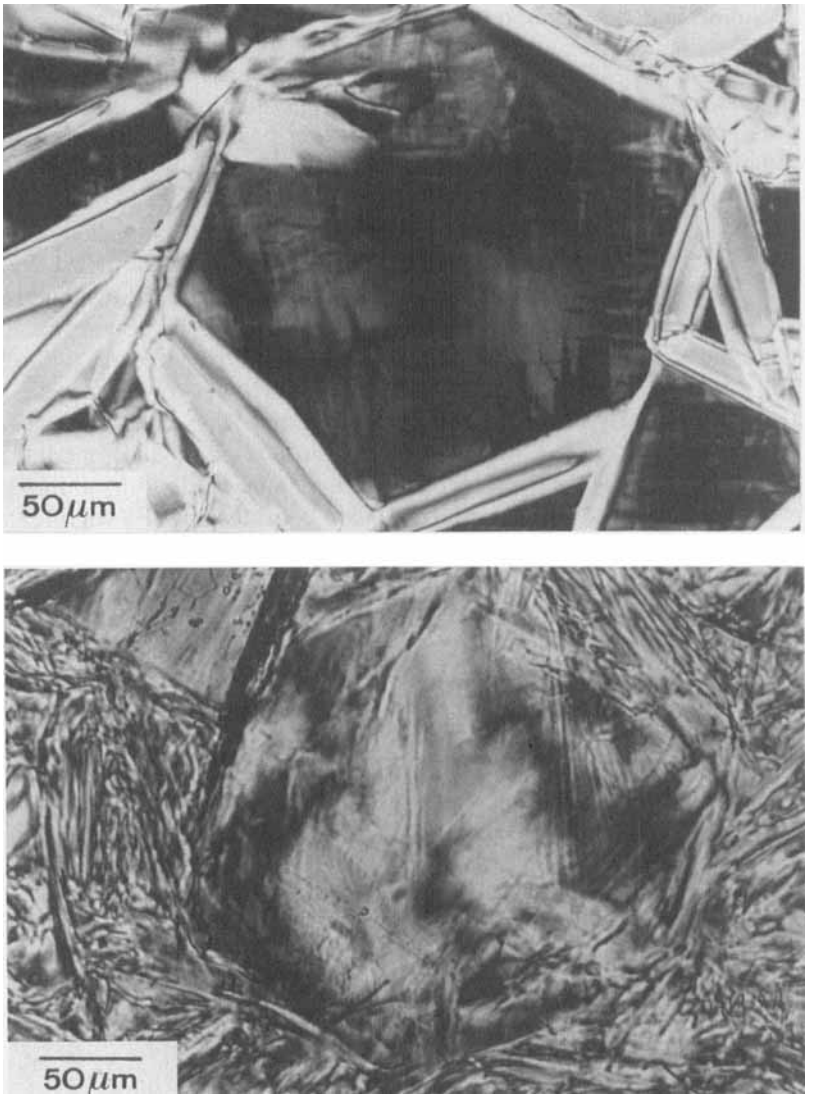

FIGURE 2 (*Continued*)
See Color Plate II.

rocarbon-hydrocarbon alkanes. A broader range of the smectic state was also observed for semifluorinated allyl ethers.[11] While for the latter a liquid crystalline structure of the smectic B type was observed, the mesomorphic phases found for the methacrylates show a higher degree of order.

d. Solution and Association Behavior

Dissolution studies revealed that the solubility of the semifluorinated methacrylates in organic solvents surpasses that of the unfunctionalized molecules[6] and also that of the semifluorinated allyl ethers.[11] We ascribe this at least partly to a better interaction with the solvent. Also the bulky methacrylate group may hinder crystallization.

Surface tension effects in solutions of different perfluoroalkyl-alkylene methacrylates were determined using the Wilhelmy plate method. 1,1,2,2-Tetrachloroethane was chosen as solvent, because it dissolves the semifluorinated compounds rather well and is also a selective solvent for the hydrocarbon segment.[11]

When the solution was freshly filled into the measuring trough, rather high values for the surface tension were measured at first. However, the surface tension decreased continuously and after equilibration times of typically 2 h, the values given in Figure 3 were reached. Once a low energy surface layer had formed, the Wilhelmy plate could be removed carefully, cleaned in a flame, and redipped into the solution without increasing the actual surface tension considerably. By stirring the solution, however, the surface tension value observed at the start of the measurement was restored, and then decreased again during the next few hours.

As shown in Figure 3, a significant decrease in the surface tension was observed in all cases at rather low concentrations. The lowest surface tension and the steepest slope in the surface tension *versus* concentration plot was obtained with the compound having the longest solvent-incompatible fluorocarbon segment. Above a

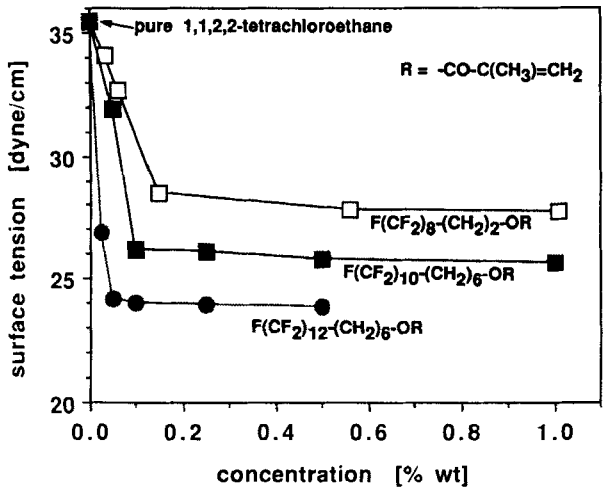

FIGURE 3 Surface tension plotted *vs.* concentration for solutions of perfluoroalkyl-alkylene methacrylates in 1,1,2,2-tetrachloroethane.

"critical concentration" of 0.15% weight, 0.10% weight, and 0.06% weight for the methacrylates carrying a C_8-, C_{10}-, and C_{12}-fluorocarbon segment, respectively, addition of more perfluoroalkylalkylene methacrylate did not reduce the surface tension to any considerable further degree. Thus the data clearly show that the semifluorinated methacrylates form a surface layer at the solution/air interface.

A similar behavior was observed for solutions of sequentially perfluorinated allyl ethers using the same solvent.[11] However, in this case only molecules with a C_{12}-fluorocarbon segment gave a strong decrease in the surface tension. Thus, the surface activity is more pronounced in the case of the methacrylates, where, even at low concentrations, the C_8- and C_{10}-fluorocarbon substituted molecules also effectively reduced the surface tension.

The intersection of the two straight lines by which the surface tension-concentration dependence can be fitted, might be understood as a critical micelle concentration (CMC). Observation of a CMC is based on equilibrium between monomeric and multimeric species. Typically, in aqueous solutions of surfactants, micelle formation is observed only after a monolayer of the surfactant is formed at the liquid/air interface. However, micelle formation represents a liquid-liquid segregation which should be spontaneous after passing the critical conditions. This was not the case in the strongly time dependent surface tension experiments on perfluoroalkyl substituted methacrylates. So it must be noted that little is still known about the nature of the aggregation and surface activity of fluorocarbon-hydrocarbon amphiphiles in organic solution.

Association was observed in various fluorocarbon solvents by solubilization experiments.[8] By light scattering experiments in hydrocarbon solvents, clear association was found.[6] Other experiments with different fluorocarbon-hydrocarbon compounds demonstrated strong angular dependences of the scattered light, in combination with relatively small apparent M_w values, pointing to the coexistence of very large particles with dispersed monomeric molecules. Again, large time dependent variations were observed. Retardation in the lowering of the surface tension and the formation of aggregates might be interpreted as suggesting a nucleated process such as crystallization. So it should be considered that the observed effects might be due to the formation of ultra-small soluble crystallites.

e. Gel-Formation

Extremely thin and long crystals are formed when fluorocarbon-hydrocarbon compounds crystallize from hydrocarbon or fluorocarbon solution. The crystals can build up a fine network which encloses large solvent fractions in the cavities. Macroscopically, a solidification of the whole system is observed and an opaque gel is formed.[6,23–25] Solutions containing as little as 2% wt. of an alkane with a perfluorododecyl substituent gave rather rigid gels at room temperature.[6]

The size of the crystals which build up the network and the number of crystallites per volume depend on the crystallization conditions. By polarizing microscopy on perfluoroalkyl-alkylene methacrylates we found that fast cooling by quenching of the homogeneous solution in liquid nitrogen results in multiple nucleation and networks with a smaller mesh size than those obtained by slow cooling. However, no submicroscopic structures were obtained from the methacrylate systems. Such

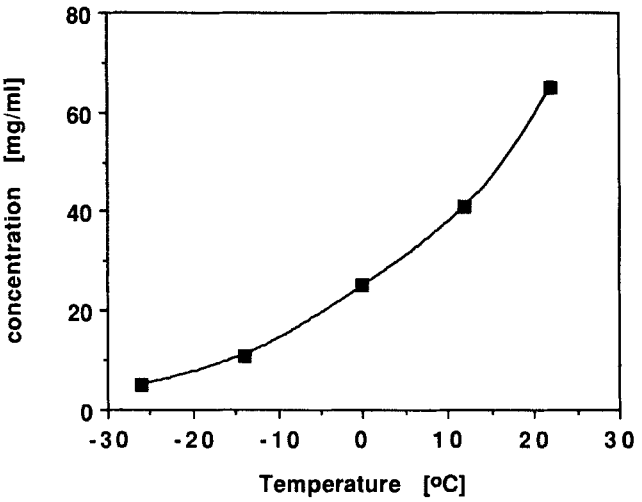

FIGURE 4 Temperature dependence of the critical concentration for gelation of solutions of $F(CF_2)_{12}(CH_2)_6$—OOC—$(CH_3)C{=}CH_2$ in toluene. For cooling conditions see text.

nanometer structures were observed in the case of non-functionalized semifluorinated alkanes.[6,26] Also methacrylates formed only relatively short needles, while extremely large aspect ratios of the crystallites were obtained by slow cooling of the corresponding alkanes. The enhanced solubility of fluorocarbon-hydrocarbon molecules with functional groups at the end of the hydrocarbon segment causes a strong increase in the minimal concentrations necessary to yield gel formation. In Figure 4, the critical concentrations for the gelation of toluene solutions of $F(CF_2)_{12}$—$(CH_2)_6$—$OCH_2CH{=}CH_2$ are plotted *versus* the temperature. Mixtures were homogenized at 70°C in test tubes which were then placed in differently thermostated baths as indicated in Figure 4. Gel formation was strongly retarded when the mixtures were slowly cooled in thermostated baths at a rate of 2 K/min, but no significant change in the critical concentration values was noted.

While solutions of the methacrylate with a perfluorododecyl segment gave gels at room temperature above a concentration of 6% wt., the corresponding compound $F(CF_2)_{10}$—$(CH_2)_6$—$OCH_2CH{=}CH_2$, with a shorter solvent incompatible segment, stayed in homogeneous solution even at a concentration of 30% wt. At −26°C, 20% wt of the methacrylate was needed for the formation of a rigid gel, while at lower concentrations, the system became highly opaque, but stayed liquid.

CONCLUSIONS

Molecules in which fluorocarbon and hydrocarbon segments are linked together organize into lamellar structures in the crystalline state as well as in liquid crystalline phases. The incorporation of a methacrylic functional group at the end of the hydrocarbon segment causes a widening of the temperature range of the liquid crystalline state. Compared to semifluorinated alkanes without a functional group,

smectic phases with a higher degree of order are formed. This might be explained by polar interactions between the methacrylate groups in the lamellar structures. The presence of the methacrylate groups also enhances the solubility of the semifluorinated compounds in organic solvents. The surface activity caused by the amphiphilic character of the fluorocarbon-hydrocarbon compounds demonstrates molecular organization within the solution/air interface. It cannot be decided whether this is analogous to the effects observed for conventional surfactants in aqueous solution. The time dependence which was observed might indicate that formation of soluble particles is involved.

Introduction of the polymerizable methacrylic groups in the peculiar lamellar structures of fluorocarbon-hydrocarbon molecules directs the interest towards the polymerization of these monomers in the pre-ordered state. The resulting stabilization of the supermolecular structure in a polymeric system represents a route to novel organic materials with special properties. Polymerization of fluorocarbon-hydrocarbon methacrylates organized in the microcrystallite gel state, giving highly porous materials with ordered fluorocarbon surfaces, will be discussed in a forthcoming article.[15]

References

1. J. F. Rabolt, T. P. Russell and R. J. Twieg, *Macromolecules*, **17**, 2786 (1984).
2. T. P. Russell, J. F. Rabolt, R. J. Twieg, R. L. Siemens and B. L. Farmer, *Macromolecules*, **19**, 1135 (1986).
3. C. Viney, T. P. Russell, L. E. Depero and R. J. Twieg, *Mol. Cryst. Liq. Cryst.*, **168**, 63 (1989).
4. J. Höpken and M. Möller, submitted to *Macromolecules*.
5. W. Mahler, D. Guillon and A. Skoulious, *Mol. Cryst. Liq. Cryst. Lett.*, **2**, 111 (1985).
6. J. Höpken, C. Pugh, W. Richtering and M. Möller, *Makromol. Chem.*, **189**, 911 (1988).
7. C. Pugh, J. Höpken and M. Möller, *Polym. Prepr.*, (*Am. Chem. Soc., Div. Polym. Chem.*), **29(1)**, 460 (1988).
8. M. P. Turberg and J. E. Brady, *J. Am. Chem. Soc.*, **110**, 7797 (1988).
9. H. R. Brown, *Macromolecules*, **22**, 2859 (1989).
10. F. Franks, "*Water. A Comprehensive Treatise.*" Vol. 4, Plenum Press, New York, 1975.
11. J. Höpken, M. Möller and S. Boileau, *New Polymeric Mater.*, **2**, 339 (1991).
12. H. Ringsdorf, B. Schlarb and J. Venzmer, *Angew. Chem.*, **100**, 117 (1988).
13. B. Lühmann and H. Finkelmann, *Colloid Polym. Sci.*, **265**, 506 (1987).
14. H. Finkelmann, *Angew. Chem.*, **99**, 840 (1987).
15. J. Höpken and M. Möller, in preparation.
16. A. Hassner and V. Alexian, *Tetrahedron Lett.*, **46**, 4475 (1978).
17. K. H. Illers, *Eur. Polym. J.*, **10**, 911 (1974).
18. N. O. Brace, *J. Org. Chem.*, **38**, 3167 (1973).
19. W. P. Neumann, *Synthesis*, 665 (1987).
20. L. H. Holmsley, "*Azeotropic Data*," *Advances in Chemistry Series*, Vol. 6, American Chemical Society, New York, 1952.
21. E. F. V. Scriven, *Chem. Soc. Rev.*, **12**, 129 (1983).
22. G. W. Gray and J. W. Goodby, "Smectic Liquid Crystals," Leonard Hill, Glasgow, 1984.
23. W. Mahler, private communication.
24. R. J. Twieg, T. P. Russell, R. L. Siemens and J. F. Rabolt, *Macromolecules*, **18**, 1361 (1985).
25. J. F. Rabolt, T. P. Russell, R. L. Siemens, R. J. Twieg and B. L. Farmer, *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*), **27(1)**, 223 (1986).
26. J. Höpken, H. Künstle and M. Möller, submitted to Colloid Polym. Sci.