

Synthesis of poly(vinyl ether)s with perfluoroalkyl pendant groups

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SUMMARY:

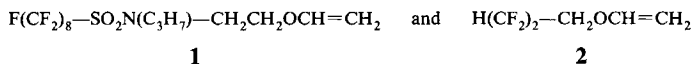
2-Perfluoro(alkyl)ethyl vinyl ethers, $F(CF_2)_nCH_2CH_2OCH=CH_2$, ($n = 6$ or 8), were synthesized and polymerized by means of cationic initiators (HI/ZnI_2 and $CF_3SO_3H/(CH_3)_2S$). The perfluorohexyl-substituted poly(vinyl ether) is completely amorphous. The polymer with perfluorooctyl segments shows side chain crystallization with a disordering transition. For the corresponding perfluorooctyl monomer a liquid-crystalline phase was observed before melting. Copolymerization experiments of the fluorocarbon-segmented monomers with a vinyl ether containing a cyanobiphenyl group in the side chain did not give homogeneous copolymers. This is attributed to the slower rate of polymerization of the fluorinated vinyl ethers as compared with the liquid-crystalline comonomer.

Introduction

The discovery of "living" cationic polymerization of alkyl vinyl ethers has led to the preparation of well-defined poly(vinyl ether)s, including block-copolymers and end-functionalized polymers¹⁾. New initiator systems allow the controlled polymerization of vinyl monomers having pendant polar and unsaturated functional groups²⁾. The rate of the propagation reaction is strongly influenced by the electron density in the vinyl double bond which therefore determines the polymerizability of the respective vinyl monomer³⁾. While electron-donating pendant groups increase the stability of the carbocationic species and the propagation rate constant, monomers carrying electron-withdrawing substituents destabilize the growing carbocation, which causes chain transfer, termination and other side reactions⁴⁾.

This work is directed towards the synthesis and polymerization of monomers carrying a fluorocarbon segment. Such molecules have an amphiphilic character, which results in peculiar bulk and solution properties^{5,6)}. Recently, we have shown that fluorocarbon-hydrocarbon diblock molecules are surface active and assemble to form soluble aggregates in non-aqueous solution^{7,8)}. Polymerization of such diblock molecules may lead to a stabilization of the selforganization, as it was observed for nonionic surfactants⁹⁾. Thus, polymer materials with special morphologies and surface properties are expected to be formed.

As perfluoroalkyl groups are strongly electron-withdrawing moieties, the cationic polymerization of vinyl ethers with fluorocarbon substituents is expected to be difficult. In addition, insolubility of perfluoroalkyl-substituted polymers in common organic solvents may cause precipitation of the polymer during the reaction, as it was observed by Higashimura et al.¹⁰⁾ who polymerized



by initiation with $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ or HI/ZnI_2 . While **1** could be polymerized to 100% conversion in trichlorotrifluoroethane solution, the polymer formed from **2** precipitated at conversions above 30%. The rate constant for the propagation step of the polymerization of **1** and **2** depends on the efficiency of the electronic decoupling of the electron-withdrawing fluoroalkyl group from the vinyl ether function¹⁰⁾. Monomer **1**, with two methylene units in between the perfluoro(alkyl)sulfoamino segment and the vinyl ether function, polymerized about ten times faster than **2** with only one insulating methylene unit, but still considerably slower than standard alkyl-substituted vinyl ether monomers.

In this communication we report on the synthesis and cationic polymerization of 2-perfluoro(alkyl)ethyl vinyl ethers $\text{F}(\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OCH}=\text{CH}_2$. Monomers with $n = 6$ and $n = 8$ were homopolymerized and also copolymerized with a mesogenic vinyl ether. While the preparation of the monomer with $n = 6$ has been described recently by Boutevin and Youssef¹¹⁾, to our knowledge no report about the polymerization of this type of vinyl ether monomers has appeared yet.

Experimental part

Materials: 1*H*,1*H*,2*H*,2*H*-Perfluoroalkyl alcohols (i. e. 2-perfluoro(alkyl)ethanols) (Fluorchem), 1,10-phenanthroline (Janssen), palladium(II) acetate (Merck) and anhydrous dimethyl sulfide (99%; Aldrich), were used as received. Ethyl vinyl ether (99%; Merck), chloroform and 1,1,2-trichlorotrifluoroethane (F113, Fluka) were distilled over calcium hydride. 1,10-Phenanthrolinepalladium(II) diacetate was synthesized according to a literature procedure¹²⁾.

Dichloromethane, used as a polymerization solvent, was first stirred with concentrated sulfuric acid until the acid stayed colourless, then washed with water, dried over magnesium sulfate, refluxed over calcium hydride and freshly distilled before use. Anhydrous and iodine-free hydrogen iodide gas was generated by heating a mixture of iodine and tetrahydronaphthalene to 453 K and passing the generated gas first over phosphorus pentoxide and then through a short column filled with red phosphorus. Under exclusion of light, the hydrogen iodide was dissolved in hexane freshly distilled from potassium and stored at 245 K. The activity of this initiator solution was determined by extracting a sample with distilled water and titrating the aqueous solution with sodium hydroxide and bromothymol blue as the indicator. Zinc iodide (99,99%; Aldrich), which is also very light-sensitive, was finely ground and dissolved in dry ether (2 mg/mL) in the dark and stored at 245 K. Trifluoromethanesulfonic acid (triflic acid, 98%; Fluka) was distilled under nitrogen.

11-(4-Cyano-4'-biphenyloxy)undecanyl vinyl ether was prepared as described previously¹²⁾.

1H,1H,2H,2H-Perfluorooctyl vinyl ether and *1H,1H,2H,2H-perfluorodecyl vinyl ether*: 30 mmol of 1*H*,1*H*,2*H*,2*H*-perfluoroalkyl alcohol was added to a mixture of 100 mL of dry ethyl vinyl ether, 100 mL of dry chloroform and 2 mmol (0,8 g) of 1,10-phenanthrolinepalladium(II) diacetate and kept under nitrogen. The yellow mixture slowly turned green while it was refluxed

for 12 h. After filtration, the solvent was removed in a rotavapor apparatus. The crude product was purified from unreacted fluorinated alcohol and traces of the formed ethanol by flash chromatography through a short column filled with basic alumina using ether as the solvent. After evaporation of the solvent the vinyl ethers were distilled under reduced pressure.

$F(CF_2)_6CH_2CH_2-O-CH=CH_2$: purity 99,6% (GC); m. p. 243 K; b. p. 327 K (at 12 mm Hg).

1H NMR ($CDCl_3$): $\delta = 2,51$ (tt; $-CF_2-CH_2-$, 2H; $J_{H-F} = 18$ Hz, $J_{H-H} = 6$ Hz), 4,00 (t; $-CF_2-CH_2-CH_2-O-$, 2H), 4,10 (d; *trans*- $\underline{H}-CH=CH-O-$, 1H; $J = 6$ Hz), 4,23 (d; *cis*- $\underline{H}-CH=CH-O-$, 1H; $J = 14$ Hz), 6,47 (q; $CH_2=CH-O-$, 1H).

$F(CF_2)_8CH_2CH_2-O-CH=CH_2$: purity 99,5% (GC); disordering transition 232 K; m. p. 266 K; b. p. 344 K (at 3 mm Hg).

1H NMR ($CDCl_3$): $\delta = 2,51$ (tt; $-CF_2-CH_2-$, 2H; $J_{H-F} = 18$ Hz, $J_{H-H} = 6$ Hz), 4,00 (t; $-CF_2-CH_2-CH_2-O-$, 2H), 4,10 (d; *trans*- $\underline{H}-CH=CH-O-$, 1H; $J = 6$ Hz), 4,23 (d; *cis*- $\underline{H}-CH=CH-O-$, 1H; $J = 14$ Hz), 6,47 (q; $CH_2=CH-O-$, 1H).

Cationic polymerizations were performed under a nitrogen atmosphere at 273 K for 2 h in a two necked flask equipped with a teflon stopcock and a rubber septum. All reactants were transferred into the flask by means of a syringe. Liquid monomers were distilled from calcium hydride before use. In the case of the copolymerizations of a fluorinated vinyl ether and the mesogenic vinyl ether, the solid monomer was dried in the polymerization flask by applying vacuum (10^{-2} mmHg) overnight. The polymerization was carried out in the dark, when the HI/ZnI_2 initiator was used.

Subsequently, a solution of HI in hexane and a solution of ZnI_2 in ether were added to a 10 vol.-% solution of the monomer(s) in the polymerization solvent. The monomer/initiator mole ratio was 100, and the mole ratio of initiator/Lewis base was 25. In case of the polymerizations with the triflic acid/dimethyl sulfide initiator system, the Lewis base was injected first in a 10:1 mole ratio with respect to the initiator.

Tab. 1. Polymerization and copolymerization experiments of fluorocarbon-segmented vinyl ethers

Sample	Mono- mer(s) ^{a)}	Solvent	Initiator system	Polymer yield ^{b)} in wt.-%	\overline{DP}_n ^{c)}	Copolymer composition ^{d)} in mol.-%
Homopolymers:						
1	A	CH_2Cl_2	$TfOH^e)/(CH_3)_2S$	25 ^{f)}	35	
2	A	F113 ^{g)}	HI/ZnI_2	71	75	
3	B	F113	HI/ZnI_2	62	55	
4	B	F113	$TfOH^e)/(CH_3)_2S$	67	40	
Copolymers:						
5	A/C	CH_2Cl_2	$TfOH^e)/(CH_3)_2S$	58	30	47/53
6	B/C	CH_2Cl_2	$TfOH^e)/(CH_3)_2S$	77	20	40/60
Ref. 12)	C	CH_2Cl_2	$TfOH^e)/(CH_3)_2S$	72	20	100

a) A: $F(CF_2)_6CH_2CH_2OCH=CH_2$, B: $F(CF_2)_8CH_2CH_2OCH=CH_2$,
C: $NC-C_6H_4-C_6H_4-O(CH_2)_{11}OCH=CH_2$.

b) After purification.

c) Number average degree of polymerization from 1H NMR.

d) From 1H NMR.

e) $TfOH$: Trifluoromethanesulfonic acid.

f) Polymer precipitated during polymerization.

g) 1,1,2-Trichlorotrifluoroethane (Freon 113).

After 2 h, the reaction was quenched with $\text{CH}_3\text{OH}/\text{NH}_4\text{OH}$ (3:1), and the polymer was precipitated in 75 mL of methanol. The polymer was precipitated in 75 mL of methanol. It was collected and reprecipitated from F113 solution into methanol. Reaction conditions and polymerization results are summarized in Tab. 1.

^1H NMR spectra were recorded on a Varian XL-200 spectrometer in CDCl_3 or in mixtures of CDCl_3 and 1,1,2-trichlorotrifluoroethane (F113) at 293 K, using the CHCl_3 signal ($\delta = 7,26$) and the tetramethylsilane (TMS) signal ($\delta = 0$) as internal standards.

Thermal analysis was performed on a Perkin-Elmer DSC-7 equipped with a PE-7700 computer and TAS-7 software. The phase transition temperatures are given as measured with a heating rate of 10 K/min. Glass transition temperatures as determined by the point of inflection in the heat capacity step were extrapolated to heating rate zero¹³. Cyclohexane, gallium and indium were used as calibration standards.

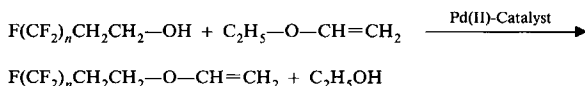
Optical polarization microscopy was done with a Leitz Ortholux II Pol BK microscope equipped with a Mettler FP 82 hot stage.

Gas chromatography was done on a Varian 3700 equipped with a two meter 22,5% QF-1 column using helium as carrier gas at temperatures between 80 °C and 180 °C.

Gel permeation chromatography was performed using DuPont SE100, SE500 and SE1000 columns. Chloroform was the solvent, and the flow rate was 2 mL/min. A Waters 411 differential refractometer, a Beckmann UV-detector operating at 254 nm and a Chromatix KMX-6 low-angle laser light scattering (LALLS) apparatus operating at a scattering angle of 6,5° were used simultaneously for the detection of the polymer fractions.

Results and discussion

Vinyl ethers with a fluorocarbon substituent were synthesized by transesterification of perfluoro(alkyl)ethyl alcohols with ethyl vinyl ether.



Catalyzed with 1,10-phenanthroline palladium(II) diacetate, the equilibration reaction can be performed under mild conditions^{11,14}. The equilibrium was shifted to the side of the fluorinated ether by use of a vast excess of ethyl vinyl ether. The low boiling points of ethyl vinyl ether and ethanol, which is formed during the reaction, facilitated the purification of the product. The remaining fluorinated alcohol was removed from the equilibrium mixture by flash chromatography through basic alumina.

Thermal analysis revealed that $\text{F}(\text{CF}_2)_8\text{CH}_2\text{CH}_2\text{—O—CH=CH}_2$ undergoes a disordering transition at 232 K before melting occurs at 264 K. No mesomorphic transition was found for $\text{F}(\text{CF}_2)_6\text{CH}_2\text{CH}_2\text{—O—CH=CH}_2$ (m. p. 243 K). The stepwise melting of $\text{F}(\text{CF}_2)_8\text{CH}_2\text{CH}_2\text{—O—CH=CH}_2$ corresponds to the behavior reported for diblock molecules with longer fluorocarbon and hydrocarbon segments^{5–8}. For $\text{F}(\text{CF}_2)_{12}(\text{CH}_2)_n\text{H}$ ($n = 4–14$), it was demonstrated that the hydrocarbon segments lose their conformational uniformity and attain a liquid-like dynamic conformational equilibrium state at the transition to the mesomorphic state. Regularity is retained in the packing of the fluorocarbon segments. Differences in the order and the motional states of the two segments are a consequence of their incompatibility which leads to the formation of peculiar double-layered morphologies in the crystals of fluorocarbon-hydrocarbon diblock molecules^{6,8,15,16}.

The polymerizable vinyl ether function at the end of the hydrocarbon segment provides a key to the preparation of new polymeric materials. Cationic polymerization of the fluorine-containing vinyl ethers was initiated with HI/ZnI₂ or with trifluoromethanesulfonic acid/dimethyl sulfide (TfOH/Me₂S). Both initiator systems induce living polymerization of alkyl vinyl ethers^{17,18}. While triflic acid and dimethyl sulfide were easy to purify and to handle, the preparation and handling of solutions of the light-sensitive, iodine-containing compounds required much more care. Polymers were obtained with both initiator systems after only two hours of reaction at 273 K. The obtained products were characterized by ¹H NMR and differential scanning calorimetry (DSC) measurements. Gel permeation chromatography (GPC) analysis could only be done for the copolymers due to the insolubility of the homopolymers in common organic solvents.

In a first experiment we used methylene dichloride as solvent for the homopolymerization of F(CF₂)₆CH₂CH₂—O—CH=CH₂. However, during the reaction the polymer precipitated as a sticky oil (see Tab. 1, sample 1). 1,1,2-Trichlorotrifluoroethane (F113) was used as solvent in the subsequent homopolymerization experiments, and no polymer precipitation was observed (samples 2–4). Copolymerizations of the fluorinated vinyl ethers with 11-(4-cyano-4'-biphenyloxy)undecanyl vinyl ether were conducted in methylene dichloride solution because the cyanobiphenyl compound did not dissolve in F113 (samples 5 and 6). The two monomers were fed to the reaction in equal amounts.

Tab. 1 summarizes the polymerization results. In the first experiment, the precipitation of the polymer in the unsuitable reaction solvent caused a very low yield. In the other cases, the deviation from 100% polymer yield is mainly due to losses during the purification.

The number-average degree of polymerization shown in Tab. 1 was estimated from the ¹H NMR spectra of the polymers. Fig. 1 shows the spectrum obtained for the polymer of F(CF₂)₆CH₂CH₂—O—CH=CH₂. The resonance of the acetal proton (—CH(OCH₃)—CH₂CH₂—(CF₂)_nF) which was formed by quenching the polymeric carbocation with methanol can be clearly distinguished at $\delta = 4,78$ ¹⁹. The integral of this peak is a measure of the number of polymer chains (provided no chain termination occurs during polymerization) and may be correlated with the number of repeating units represented by the integral of the resonance of the methylene protons in the polymer main chain (at $\delta = 1,62$). In case of the copolymerization experiments of a fluorinated vinyl ether with 11-(4-cyano-4'-biphenyloxy)undecanyl vinyl ether, this resonance is covered by the peak originating from the methylene units of the undecanyl spacer (Fig. 2). Here, the sum of the integrals of the resonance of the methylene unit neighboring the fluorocarbon segment (at $\delta = 2,36$) and of the aromatic protons in the other comonomer can be taken as a measure for the overall number of repeating units, and the ratio of the intensity of these resonances indicates the relative fraction of each comonomer in the obtained materials.

GPC analysis was performed for the copolymers which were soluble in chloroform (samples 5 and 6). Fig. 3 shows the detector signals vs. elution volume plotted for the 1 : 1 copolymer from perfluoro(hexyl)ethyl vinyl ether and 11-(4-cyano-4'-biphenyloxy)undecanyl vinyl ether. While the UV-detector measuring the absorption at 254 nm

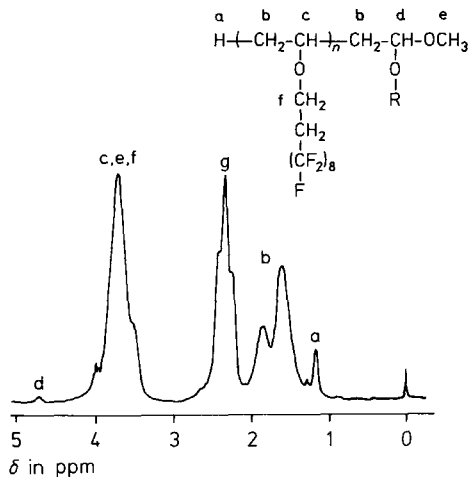


Fig. 1. ^1H NMR spectrum of poly[perfluoro(hexyl)ethyl vinyl ether] recorded from a solution in a mixture of F113 and CDCl_3

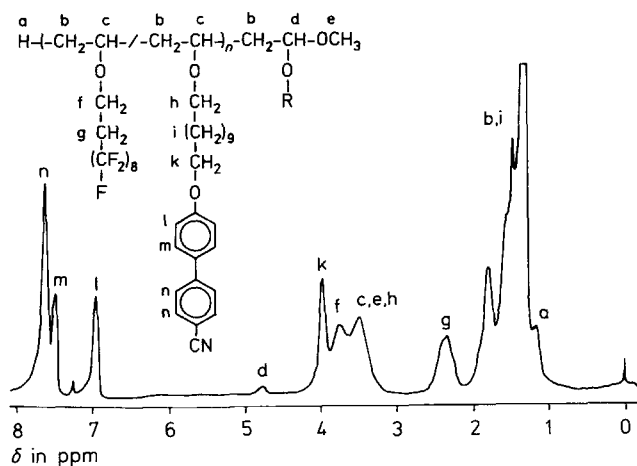


Fig. 2. ^1H NMR spectrum of poly[perfluoro(octyl)ethyl vinyl ether-co-11-(4-cyano-4'-biphenyloxy)undecanyl vinyl ether] recorded in CDCl_3 solution

and the low-angle laser light scattering (LALLS) detection showed only one peak at an elution volume of 30 mL, the refractive index detector denoted first a fraction with a higher refractive index at 30 mL, followed by a second fraction having a lower refractive index than the pure solvent at 35 mL elution volume.

Because fluorine-containing molecules have very low refractive indices, it can be concluded that the composition of the copolymer is not homogeneous. The increase of the refractive index at 30 mL corresponds to the elution of a polymer fraction

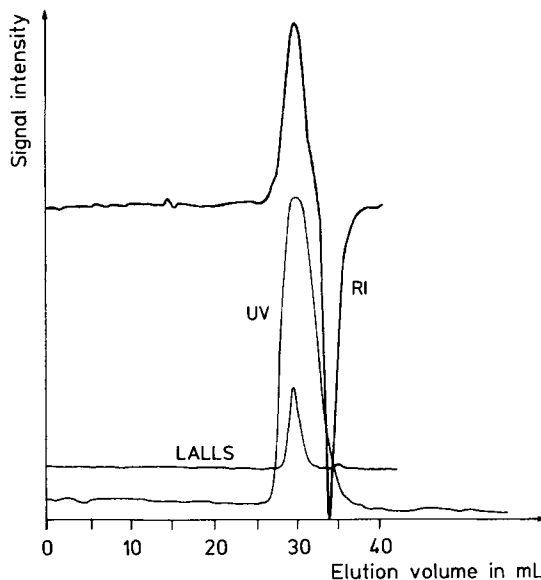


Fig. 3. GPC traces of the polymer obtained from the copolymerization of perfluoro(hexyl)ethyl vinyl ether and 11-(4-cyano-4'-biphenyloxy)undecanyl vinyl ether. (LALLS: low-angle laser light scattering, UV: ultra-violet photometry, RI: refractive index detection)

consisting predominantly of the cyanobiphenyl-containing repeating units, while the drop of the refractive index below the value observed for pure chloroform at 35 mL is due to the presence of a polymer fraction containing principally fluorinated repeating units.

The UV-detector does not respond to the elution of the mostly fluorinated polymer fraction at 35 mL, because no UV-absorbing functional groups are present in the molecular structure. Because of the extremely small value for the refractive index increment (dn/dc) for chloroform solutions of sequentially fluorinated poly(vinyl ethers), only a very small light scattering signal could be detected.

A strong influence of the length of the fluorocarbon segments in the side chains resulted also for the thermal behavior of the homopolymers (see Tab. 2). The homopolymer containing perfluorohexyl groups was found to be completely amorphous with a glass transition temperature of 231 K. Optical polarization microscopy proved that the material is isotropic above 248 K, which is the low-temperature limit of our equipment. Obviously, side chain crystallization does not take place. In contrast, crystallization was found for the polymer containing perfluorooctyl segments. In the first heating scan the precipitated polymer showed a very weak disordering transition at 296 K followed by an isotropization at 314 K. After fast cooling, a weak T_g at 265 K was found in the second heating scan. The disordering transition at 296 K now accounted for about 75% of the much smaller total liberated entropy, and isotropization occurred already at 303 K. Thus, two differently ordered states of the fluorocarbon segments are indicated. A perfect three-dimensional crystalline packing is not expected even at very low temperatures because of the bonding to the non-stereoregular main chain. It can not be said what kind of further disordering occurs at the transition observed in the DSC experiments. The textures

Tab. 2. Thermal transitions of the obtained polymers (T_g : glass transition temperature; T_d : disordering trans. temp.; T_i : isotropization temp.; mru: mol of repeating units)

Sample	Mono- mers ^{a)}		T_g /K	T_d /K	$\frac{\Delta H_d}{\text{(kJ/mru)}}$	T_i /K	$\frac{\Delta H_i}{\text{(kJ/mru)}}$
Homopolymers:							
1 + 2	A	1st ^{b)}	231	—	—	—	—
		2nd ^{b)}	231	—	—	—	—
3 + 4	B	1st	—	296	0,3	314	8,9
		2nd	265	296	4,3	303	1,4
Copolymers:							
5	A/C	1st	—	332	16,4	391	2,5
		2nd	271	—	—	392	2,6
6	B/C	1st	—	333	17,2	396	3,0
		2nd	271	—	—	397	2,6
Ref. ¹²⁾	C	1st	289	338	12,3	433	3,4
		2nd	288	324	7,0	421	2,9

^{a)} See Tab. 1.

^{b)} Denotes first or second DSC heating scan.

observed by polarization microscopy did not show any significant difference above and below T_d . Melting and crystallization experiments did not allow to determine whether the transition occurring at 296 K is due to a change between two different modifications or a true disordering transition.

Fig. 4 shows optical polarizing microphotographs of this polymer before (a) and after (b) annealing at 299 K. The growth of the domains of the Schlieren-texture indicates an enhanced segmental mobility in the partially disordered phase observed below the isotropization temperature. The observation that side chain crystallization occurs when a perfluorooctyl segment is present in the structure of the repeating unit of a poly(vinyl ether) is consistent with a report on the thermal characterization of siloxane polymers with pending sequentially perfluorinated groups²⁰⁾. Polysiloxanes containing perfluorohexyl segments were amorphous materials with a glass transition at 208 K, while side chain crystallization occurred for the perfluorooctyl-substituted polymer.

The thermal behavior of the materials from the copolymerization experiments (samples 5 and 6) was quite similar to that reported for the homopolymer prepared from 11-(4-cyano-4'-biphenyloxy)undecanyl vinyl ether (poly[CBUVE])¹²⁾. No T_g was found in the first heating scan. The presence of the fluorocarbon-containing polymers in the material depressed the transition temperatures observed for the homopolymer. The transition from the crystalline to the smectic phase is lowered from 338 K to 333 K and the isotropization temperature from 433 K to 396 K. For sample 6, a significant increase in the transition enthalpy was observed at the crystalline-smectic transition of the liquid-crystalline polymer. Quenching of the materials from the smectic phase to 93 K led to a suppression of the disordering transition. Instead,

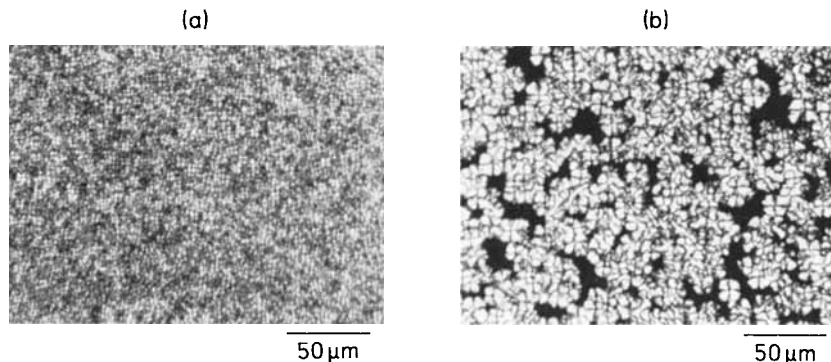


Fig. 4. Microphotographs showing the birefringence of a poly[F(CF₂)₈CH₂CH₂—OCH=CH₂] film at 299 K, cooled from the isotropic melt; (a) directly after formation of the mesomorphic phase; (b) after annealing for 8 h at 299 K

glass transitions with large changes in heat capacity were observed for both polymer systems in the second heating scan. The isotropization temperatures were not affected. It can not be decided whether the decrease in the transition temperatures compared to homopoly(CBUVE) is due to a reduced molecular weight¹²⁾ or the incorporation of fluorinated comonomers. The increase in the enthalpy of the crystalline-smectic transition may be well explained by overlap of the melting transition of fluorinated poly(vinyl ether). Also no further conclusion can be drawn from T_g because of the similarity of the glass transition temperatures of poly(perfluoro(octyl)ethyl vinyl ether) and homopoly(CBUVE).

Conclusions

Fluorocarbon-hydrocarbon molecules carrying a vinyl ether functional group can be polymerized by cationic initiation. The monomer with a perfluorooctyl segment undergoes a disordering transition before melting. Side chain crystallization with a disordering transition to a partially ordered state of enhanced mobility was observed for the corresponding polymer, while the perfluorohexyl-substituted polymer is completely amorphous.

GPC analysis showed that no homogeneous copolymers were formed in systems of fluorocarbon-segmented monomers and a vinyl ether with a liquid-crystalline, less electron-withdrawing substituent. DSC experiments showed changes in the melting behavior with respect to the liquid-crystalline poly(CBUVE) homopolymer. No phase transitions were found which can be attributed to the fluorine-containing homopolymer. Although the DSC data did not show transitions which can be assigned to different polymers, i.e. poly(perfluoro(alkyl)ethyl vinyl ether) and poly[11-(4-cyano-4'-biphenyloxy)undecanyl vinyl ether], they do not disprove the formation of a heterogeneous mixture of two different homo- or copolymers. Thus, in agreement with the slower rate of polymerization for the fluorinated vinyl ethers, it is indicated that the reactivities do not favor copolymerization.

The observed degrees of polymerization and yields demonstrate that the system is a promising candidate for living polymerization and the corresponding preparation of well defined polymers and block-copolymers. We are currently studying the living cationic polymerization of fluorocarbon-segmented vinyl ethers. Polymeric additives for the surface modification and compatibilization in polymer blend systems can be developed from block copolymers of a fluorinated and a hydrogenated vinyl ether monomer.

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