On the Bulk Properties of a Poly(Bicycloacrylate) Carrying Semifluorinated Side Groups

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Summary: We prepared a novel fluorinated polymer from a bicycloacrylate monomer, (1*H*,1*H*,2*H*,2*H*)-perfluorododecyl 2-(bicyclo[3.1.0]hex-1-yl)acrylate, by radical ring opening polymerization. The bulk properties of the polymer were investigated by thermal analysis and X-ray diffraction, which proved the existence of a smectic mesophase up to the isotropization temperature of 74 °C. Furthermore, a solid state NMR study was started to characterize domains with different mobility mainly by ^{13}C cross-polarization magic angle spinning and T_2 selective experiments. We found that the polymer is a homogeneous sample with the presence of dynamic motions in the kHz regime below the glass transition temperature.

Keywords: bicycloacrylate polymer; fluoropolymer; mesophase; ring opening polymerization; smectic polymer; solid state NMR

Introduction

There is at present a growing interest in polymers carrying semifluorinated chains, –$(CH_2)_m(CF_2)_nF$, as side groups.[1] When sufficiently long fluorocarbon chain segments are used ($n > 6$–8), the polymers can form thermotropic mesophases because of the self-assembly of the rodlike side groups,[2–4] which by contrast is not possible for amorphous polymers containing short, partly fluorinated groups.

We are interested in the synthesis and application of new polymers containing mesogenic fluorocarbon chain segments,[5–7] in which interplay between the bulk structure and the surface structure in thin films can be mediated by the liquid crystalline order of the fluorinated side chains.[7,8] The order and stability of the surface can result in a long-term low surface energy behavior.[9,10]

In this work we extended the synthesis to a completely new structure of fluorinated polymers from a highly reactive bicycloacrylate monomer with a fluorocarbon side chain and investigated their solid state structure and properties. Among the techniques allowing polymers to be studied in the bulk, solid state NMR spectroscopy is especially useful in probing local molecular structure, conformational order and dynamics. Therefore, we also initiated a study to identify and characterize domains with different mobilities by ^{13}C cross-polarization magic angle spinning (CP MAS) and T_2 selective experiments, as well as by ^{1}H static and MAS experiments.

Experimental part

Reagents

(1*H*,1*H*,2*H*,2*H*)-Perfluorododecanol (F10) (from Fluorochem) and all of the other commercial reagents were used without further purification. Commercially available solvents were purified following standard procedures.

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Monomers

Methyl 2-(bicyclo[3.1.0]hex-1-yl) acrylate (BCL Me). It was synthesized according to literature.[11]

2-(Bicyclo[3.1.0]hex-1-yl)acrylic acid (BCL COOH). 2.00 g (12 mmol) of BCL Me and 10 mg of 2,6-di-t-butyl-4-methyl phenol were dissolved in 30 mL of a degassed acetone/water solution (8/1 v/v). The solution was then cooled to 0 °C and 0.58 g of LiOH in 6 mL of water was added drop-wise under nitrogen. The mixture was stirred at room temperature for 5 days and then evaporated under vacuum to dryness. The residue was dissolved in water, washed with diethyl ether, cooled to 0 °C, acidified with conc. HCl to pH $\approx$ 1, washed with diethyl ether, dried over Na_2SO_4 and evaporated under vacuum. 1.68 g (92% yield) of a pale yellow crystalline solid was collected: m.p. 58 °C.

^{1}H NMR ($CDCl_3$): δ (ppm) = 6.3 and 5.7 (2H, CH_2=), 1.9–1.5 (6H, cyclopentane), 1.2 (1H, cyclopropane), 0.6 (2H, cyclopropane).

FT-IR (liquid film): $\bar{\nu}$ cm^{-1}) = 3100 (ν OH), 2937–2862 (ν C–H aliphatic), 1693 (ν C=O), 1426 (δ CH cyclic), 1359 (ν C–O acid).

(1H,1H,2H,2H)-Perfluorododecyl 2-(bicyclo[3.1.0]hex-1-yl)acrylate (BCL F10). A solution of 1.60 g (10.5 mmol) of BCL COOH, 5.93 (10.5 mmol) of F10 and 0.31 g (2 mmol) of 4-pyrrolidinopyridine (PPy) in 40 mL of anhydrous dichloromethane was cooled to 0 °C under nitrogen atmosphere. 2.17 g (10.5 mmol) of dicyclohexyl carbodiimide (DCC) dissolved in 20 mL of anhydrous dichloromethane was then slowly added. The mixture was kept under stirring at room temperature for 24 h. The precipitate formed during the reaction was filtered off and the organic solution was washed with 5% HCl, 5% $NaHCO_3$, and water and dried over Na_2SO_4. Subsequently, the solvent was evaporated under vacuum and the crude product was purified by flash chromatography on silica gel (230–400 mesh), using chloroform as eluent (R_f = 0.80) to give 4.67 g (yield 64%) of a pale yellow liquid.

^{1}H NMR ($CDCl_3$): δ (ppm) = 6.1 and 5.6 (2H, CH_2=), 4.4 (2H, $COOCH_2$), 2.5 (2H, CH_2CF_2), 1.9–1.5 (6H, cyclopentane), 1.2 (1H, cyclopropane), 0.6 (2H, cyclopropane).

^{13}C NMR ($CDCl_3$): δ (ppm) = 166 (COO), 143 (CH_2=), 126 ($\underline{C}$=COO), 123–107 ($(CF_2)_{10}$), 57 ($COO\underline{C}H_2$), 33–13 ($\underline{C}H_2CF_2$ + C in cycle).

FT-IR (liquid film): $\bar{\nu}$ cm^{-1}) = 2962–2866 (ν C–H aliphatic), 1727 (ν C=O), 1624 (ν C=C), 1367 (ν C–O ester), 1117 (ν C–F), 813 (δ CH vinylidene), 656 (ω CF_2).

Polymers

In a typical polymerization experiment, 1.5 g (2.15 mmol) of BCL F10, 11 mg of AIBN and 5 mL of trifluorotoluene (TFT) were introduced into a glass vial and degassed by several freeze-thaw cycles. After sealing under vacuum, the polymerization was carried out at 65 °C for 24 h. The polymer was purified by precipitations into methanol from TFT solutions leading to 1.47 g (98% yield) of p(BCL F10)a as a white powder.

^{1}H NMR (C_6F_6/C_6D_6 (3/1 v/v)): δ (ppm) = 4.4 (2H, $COOCH_2$), 2.7–2.4 (4H, =CCH_2 + CH_2CF_2), 2.2 (2H, =CCH_2 in cycle), 1.7–1.1 (6H, CH_2 in cycle), 0.9 (1H, CH).

^{13}C NMR (C_6F_6/C_6D_6 (3/1 v/v)): δ (ppm) = 170 (COO), 148 (C= in cycle), 124 (=$\underline{C}$COO), 123–107 ($(CF_2)_{10}$), 56 ($COO\underline{C}H_2$), 40–27 (CH + CH_2).

^{19}F NMR ($CDCl_3/CF_2ClCCl_2F$): δ (ppm) (from CF_3COOH) = −5 (3F, CF_3), −38 (2F, CH_2CF_2), −46 to −48 (14F, CF_2), −51 (2F, $C\underline{F_2}CF_3$).

FT-IR (film): $\bar{\nu}$ cm^{-1}) = 2962–2866 (ν C–H aliphatic), 1727 (ν C=O), 1624 (ν C=C), 1367 (ν C–O ester), 1133 (ν C–F), 656 (ω CF_2).

Characterizations

NMR Spectroscopy

In solution: The ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded with a Varian Gemini VXR 300 spectrometer (operating at 299.9, 75.4 and 282.2 MHz, respectively). Chemical shifts were referenced to external TMS, unless specified otherwise.

Solid state: High resolution ^{13}C and ^{1}H measurements were performed on a double channel Varian Infinity Plus 400, working at 100.56 MHz for ^{13}C and 399.88 MHz for ^{1}H. ^{1}H and ^{13}C NMR experiments were carried out at room temperature; magic angle spinning (MAS) experiments were performed spinning the sample at the optimized spinning rate of 6 kHz. Proton high power decoupling was used to acquire ^{13}C NMR spectra.

^{1}H NMR spectra were recorded with a solid echo (SE) sequence[12] with a 90° pulse of 4.2 μs, 32 scans, a recycle delay of 4 s and an optimized SE delay time τ_{SE} of 10 μs. ^{13}C cross polarization (CP) experiments with a recycle delay and contact time optimized to 4 s and 1.5 ms, respectively, were performed. Direct excitation (DE) ^{13}C spectra were recorded by using a depth pulse sequence[13] in order to suppress probe and rotor background signals, with a 90° pulse of 4.05 μs, 2000 scans and a recycle delay of 5 s.

Two modified cross polarization experiments were performed to evidence different mobility sites and magnetization transfer effects: 1) T2HCP, namely delayed CP or T2 selective sequence[14]. This sequence is a cross polarization preceded by a delay τ_D and is normally used to measure proton spin-spin relaxation times. 2) T2HSLCP, a cross polarization preceded first by a delay τ_D and then by a period of spin-lock. This sequence is used to isolate the ^{1}H-^{1}H spin diffusion magnetization effect[15] from other magnetization transfer processes.

Chemical shifts were referenced to external adamantane. A 7.5 mm CP-MAS probe head was used.

Differential Scanning Calorimetry (DSC)

Measurements were performed with a Mettler DSC-30 instrument (10 °C · min^{-1} scanning rate) that had been calibrated using standard tin, indium and zinc samples. The isotropization temperature (T_i) was recorded at the maximum temperature in the DSC enthalpic peak of the second heating cycle. The glass transition temperature (T_g) was set at the half-devitrification temperature.

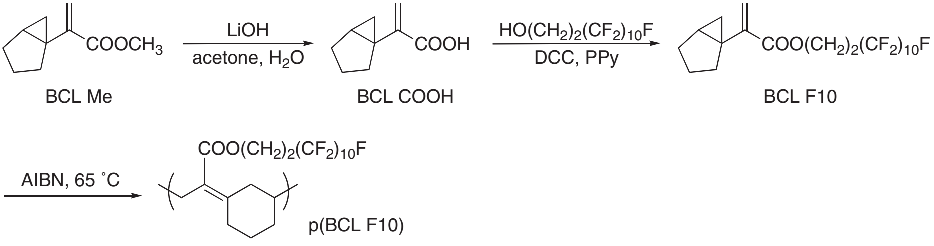
X-Ray Analysis

X-ray diffraction diagrams were recorded at LMOPS-CNRS (Vernaison – F) on powder samples with an especially designed pinhole camera using Ni-filtered Cu Kα beam (λ = 1.54 Å), under vacuum at various temperatures with an accuracy of 1 °C up to T_i.

Results and discussion

Syntheses of Monomers and Polymers

The fluorinated bicycloacrylate BCL F10 was synthesized from the methyl bicycloacrylate[11] analog (BCL Me) following a two-step pathway (Scheme 1). The methyl ester was firstly hydrolyzed under mild conditions by an aqueous LiOH solution, and the corresponding carboxylic acid was then esterified with the fluorinated alcohol



Scheme 1.
Synthesis of the fluorinated bicycloacrylate monomer BCL F10 and polymer p(BCL F10).

Table 1.
Preparation of p(BCL F10)a-d polymer samples under different conditions.

Sample	BCL F10 (mmol)	Solution[a)]	Initiator[b)]	Temp. (°C)	Time (h)	Yield (%)
p(BCL F10)a	2.15	TFT, 0.5 M	AIBN	65	24	98
p(BCL F10)b	1.07	–	AIBN	65	48	93
p(BCL F10)c	1.07	TFT, 0.2 M	BPO	100	24	98
p(BCL F10)d	1.07	TFT, 0.2 M	TBPO	120	48	63

[a)] In trifluorotoluene, or in bulk.
[b)] 1 wt-% concentration.

F10, yielding the fluorinated monomer BCL F10.

The homopolymerization of BCL F10 was obtained by free-radical polymerization (Scheme 1). The experimental conditions were varied systematically by changing the reaction parameters such as the radical initiator (AIBN, BPO or TBPO), the temperature (65, 100 or 120 °C) and the solvent (trifluorotoluene or bulk) (Table 1). The reaction yields were generally very high, indicating the high reactivity of such ring opening monomer. The p(BCL F10) polymer samples were insoluble in common organic solvents but were soluble in fluorinated solvents like 1,1,2-trichlorotrifluoroethane, trifluorotoluene or hexafluorobenzene. This insolubility did not allow evaluation of the molecular weights by size exclusion chromatography. Nonetheless, the large molecular weights determined for the p(BCL Me) homopolymer ($\overline{M}_n = 120000$, polydispersity 2.48)[11] suggest that high polymerization degrees can be reached for such bicycloacrylate polymers.

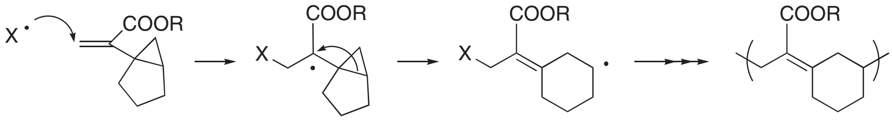
The invoked mechanism for the free radical polymerization of bicycloacrylate BCL F10 involves the ring opening of the strained cyclopropane ring (Scheme 2).[11] The initiator radical reacts with the acrylate double bond and intramolecular rearrangement of the formed radical provokes the cleavage of the C–C bridge bond, thereby yielding a six-member ring radical which can propagate and chain grow.

Consistent with this mechanism, the ^{13}C NMR spectra exhibited two signals at 148 and 124 ppm due to the C=C double bond in the polymer chain and the disappearance of the signal of the monomer cyclopropane ring at 14 ppm (Figure 1). The formation of repeat units comprised of a cyclohexane ring is likely more thermodynamically favored over that of other possible alicyclic structures via radical ring opening. Additional polymerization mechanisms may be envisioned, and this question will be addressed in a forthcoming paper.

Solid state NMR

Solid state NMR investigations were initiated on p(BCL F10) samples and p(BCL Me) that was taken as a simple polymeric model compound. We describe here our results with p(BCL F10)a as a representative polymer sample of the series. The different carbon atoms in the repeat unit were identified as is illustrated in Figure 2.

The static and MAS ^1H NMR spectra (not reported here) revealed the presence



Scheme 2.
Polymerization scheme for a bicycloacrylate monomer.

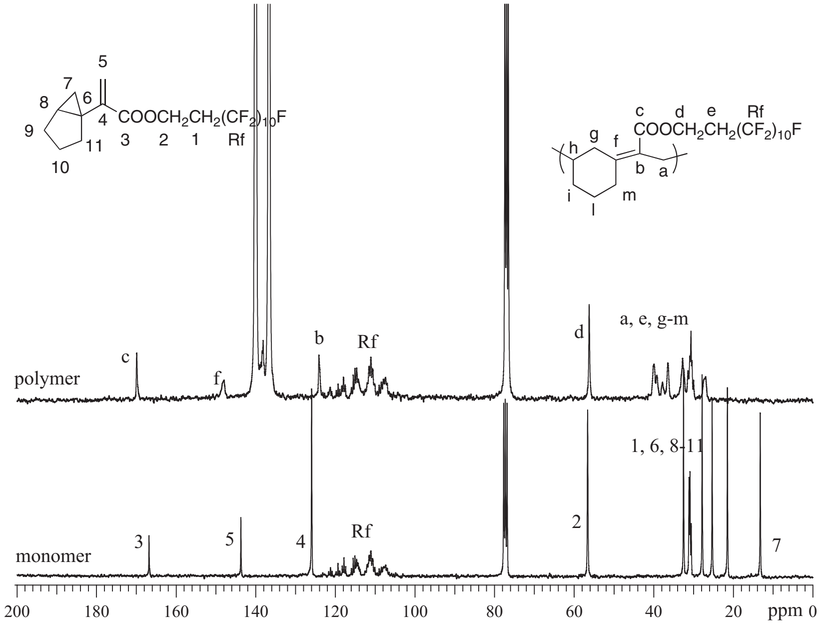


Figure 1.
^{13}C NMR spectra for BCL F10 monomer and p(BCL F10) polymer (signals at 136–142 ppm and 77 ppm are from C_6D_6/C_6F_6 and $CDCl_3$, respectively).

of a mobile part of the macromolecular structure of p(BCL F10), which clearly corresponds to the fluorinated side chains that are affected by internal reorientations. In particular, the ^{1}H MAS experiments reduced the anisotropy components of the ^{1}H-^{1}H dipolar interaction to almost zero at a spinning rate of 6 kHz, leading to a well resolved spectrum comprised of two sharp signals (with a line width, $\Delta\nu_{h/2}$of15 Hz) ascribable to the two CH_2 moieties in the side groups (positions 10 and 11 of Figure 2).

^{13}C CP-MAS NMR spectra were recorded at different contact times τ_c to identify the different carbon sites of the polymer. Several spectral regions could be distinguished (Figure 3): i) a large signal from 16 to 45 ppm corresponded to the carbons 1, 2, 4, 5, 6, and 9 in the polymer main chain and the CH_2 carbon of the side chain in the 11 position; ii) a signal at 56 ppm was due to the CH_2 carbon in the 10 position; iii) an intense and broad signal between 105 and 125 ppm was ascribed to the CF_2 signals; iv) a sharp signal at 124 ppm corresponded to the olefin carbon 7; v) a large signal at 148 ppm was from the olefin carbon 3; and vi) a signal at 170 ppm corresponded to the carbonyl carbon 8.

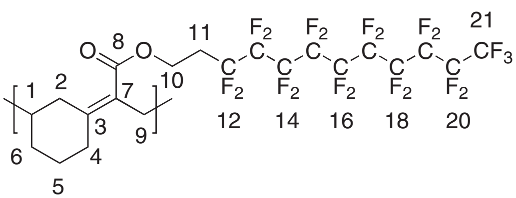


Figure 2.
Molecular structure of the repeat unit of p(BCL F10), with sites labeled according to solid state NMR explanation.

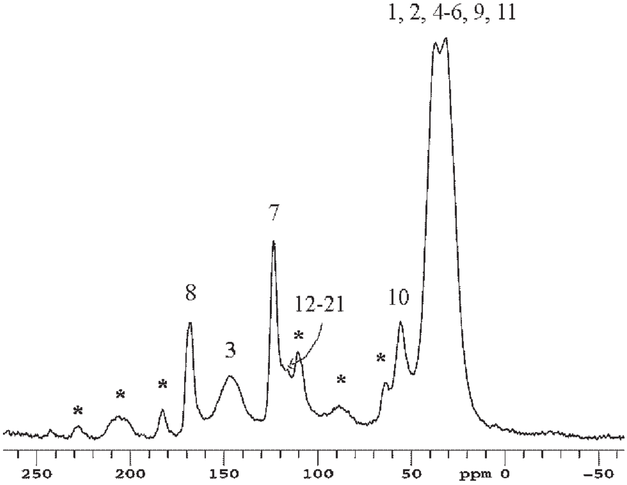


Figure 3.
^{13}C NMR CP-MAS spectrum of p(BCL F10), with a contact time of 2 ms (signals denoted by asterisks are spinning side bands).

From CP-MAS dynamic experiments with varying the contact times τ_c from 0.1 ms to 18 ms, we found that both main chain and side chain carbons were affected by motions in the kHz regime. In fact, the intensities of carbon signals showed a typical trend of systems with proton spin-lattice relaxation rates ($1/T_{1\rho}$) in the kHz regime. Moreover, the maximum cross polarization transfer was obtained at different values of contact times for each carbon moiety. The optimized τ_c was 0.5 ms for carbons 1, 2, 4, 5, 6, 9 and 11. The olefin and carbonyl carbons were characterized by longer optimized contact times, τ_c of 2–3 ms, and a less effective magnetization transfer. We also found that the CF_2 carbon linked to the CH_2 carbon in the side group was slightly affected by cross polarization transfer, with a maximum of signal intensity at τ_c of about 4 ms.

Even though the other CF_2 carbons could not be detected by ^{1}H decoupling CP MAS, they could be evidenced by using the direct excitation (DE) experiment, as is shown in Figure 4. In such experiment one

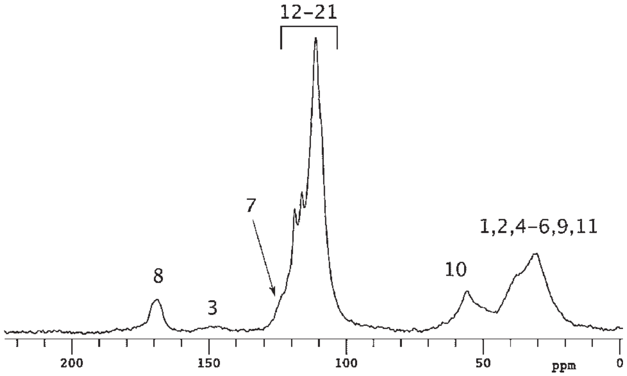


Figure 4.
^{13}C NMR DE spectrum of p(BCL F10), with a pulse delay of 5 s.

avoids all background signals and can detect directly ^{13}C signals without CP or spin diffusion transfer. By comparing the relative intensities of the signals we confirmed the carbon assignments. The signals from CF_2 carbons were the most intense and three signals could be identified from 111 ppm to 119 ppm. The olefin carbon 7 was hidden on the left side of the prominent CF_2/CF_3 band (Figure 4).

On the dynamic point of view, some preliminary results are reported to characterize regions with different mobilities. Proton T_2 selective (T2HCP) and spin-lock proton T_2 selective (T2HSLCP) experiments were carried out with the aim to identify the carbon sites and their locations in different regions.

As a main result, we observed that in the fluorinated polymer the different carbons could not be discriminated by T2HCP experiments. In fact, all signals gradually decreased in intensity with increasing delay τ_D before cross-polarizing.

However, a small spin diffusion effect was detected by applying the T2HSLCP sequence, even though this effect was much less evident for p(BCL F10) than for p(BCL Me) (Figure 5). In the latter (Figure 5 left) the spin diffusion effect from A to B signals, which correspond to the methyl side group and the main chain carbons, respectively, was pronounced and resulted to be the most important magnetization transfer phenomenon for this sample. In fact, the longer the spin-lock period before cross polarization to carbons was (0.01–3 ms), the larger the proton magnetization transfer from the methyl side group to the main chain carbons increased; see relative intensities of signals A and B in spectra 1 through 3.

For p(BCL F10) (Figure 5 right) the effect of magnetization transfer was much less effective. Here, region A corresponds to CH_2 (on position 10) of the fluorinated side group and region B includes both CH_2 and CH of the main chain and CH_2 (on position 11) of the fluorinated side group. Due to this overlap of signals in region B, it was not possible to separate unambiguously the contributions from the main chain and the side chain by varying the spin-lock period in the 0.01–0.3 ms range; see relative intensities of signals A and B in spectra 1 through 3.

The initial NMR studies suggest that the p(BCL F10) polymer is suitable for quantitative characterization of dynamic motions of the different moieties, since both the CP dynamic and T_2 selective experiments revealed the presence of dynamic components below T_g. More detailed investigations of spin-relaxation and spin-spin relaxation times are in progress.

Liquid Crystalline Behavior

The thermal and mesophase behavior of p(BCL F10) polymer samples was investi-

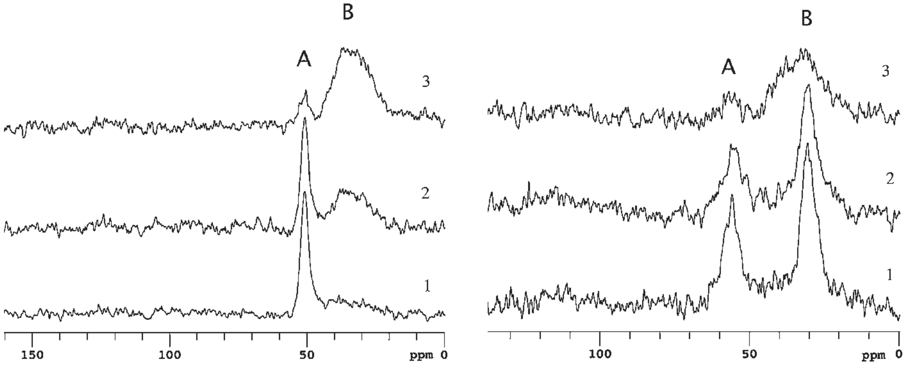


Figure 5.
^{13}C NMR spectra recorded using the T2HSLCP sequence for p(BCL Me) (left) and p(BCL F10) (right). A and B regions in the aliphatic part of spectra are shown. Spectra 1, 2 and 3 correspond to spin-lock periods of 0.01, 0.2 and 3 ms, respectively.

gated by differential scanning calorimetry and X-ray diffraction. For any polymer, the DSC glass transition temperature was identified at ~34 °C, whereas the isotropization or clearing of a liquid crystalline mesophase was detected for p(BCL F10)b only ($T_i = 74\,°C$) with an associated enthalpy ΔH_i of 0.28 $kJ \cdot mol^{-1}$. For the other polymers, there was no detectable ΔH_i, and T_i could be located at nearly the same temperature of 75 °C by X-ray studies as function of temperature. These differences in isotropization enthalpy may be due to different molecular weights of the polymer samples.

The presence of a liquid crystalline mesophase is attributed to the strong intramolecular microphase separation of the rigid rodlike fluorocarbon side groups from the chemically incompatible hydrocarbon polymer backbone.[2,10] Thus, the polymer side chains can order in greatly confined layered structures.[9,10] Smectic mesophases are in fact normally observed in polymers containing similar $-(CH_2)_m(CF_2)_nF$ side groups.[7,8] Nematic polymers appear to be rare,[8,16] the orientational and positional order of smectic mesophases being facilitated in the microphase segregated structure. The higher order of the *bulk* smectic structure can in turn induce a higher order in the *surface* smectic structure.[7,8]

The smectic mesophase was in-plane disordered and presented a layer periodicity d of 27.1 ± 0.1 Å. This structure was essentially unaffected by temperature up to T_i. Since d is much longer than the calculated maximal length L of the polymer side chains ($d/L = 1.3$), the mesogenic units should be arranged in a bilayer, partially intercalated smectic structure, like in the SmA_d mesophase.

Conclusions

A novel bicycloacrylate polymer carrying semifluorinated side groups was prepared. Assignments of ^1H and ^{13}C signals by solid state NMR techniques agree with the proposed macromolecular structure. Moreover, the polymer is a homogeneous sample with the presence of dynamic motions in the regime of kHz below T_g. The present polymer system offers a novel example of liquid crystalline polymer with a hydrocarbon-fluorocarbon structure and further confirms the distinct mesogenic character of the $-(CH_2)_m(CF_2)_nF$ chain segments, even within alicyclic repeat units that in effect widely separate the side groups from each other along the polymer backbone.

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