Notes

Rational Design of a Hexagonal Columnar Mesophase in Telechelic Alternating Multicomponent Semifluorinated Polyethylene Oligomers

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Introduction

Perfluorinated alkanes are more rigid and, due to their extremely low surface energy, less miscible than the corresponding perhydrogenated alkanes (fluorophobic effect).[1−3] Therefore, a suitable composition of a diblock or triblock low molar mass hydrocarbon containing perfluorinated and perhydrogenated segments produces a microsegregation which is responsible for the formation of highly ordered lamellar thermotropic (S_B)[4−8] and lyotropic[9] mesophases. By analogy with low molar mass compounds, alternating microblock copolymers containing perfluorinated and perhydrogenated segments also exhibit a highly ordered S_B phase.[10,11] In addition, the induction[12,13] and stabilization[14−18] of other LC phases as well as the self-assembly[19,20] of various architectures which yield LC phases *via* the semifluorination of various building blocks were subsequently reported from several laboratories. Conceptually, semifluorinated hydrocarbons are the simplest class of materials yielding LC phases, and they still present many unexplored capabilities. The first goal of this note is to report a novel synthetic method for the preparation of alternating multicomponent semifluorinated polyethylene with controlled chain ends. The second goal is to use this method for the rational design of the first semifluorinated polyethylenes which exhibit a nonlamellar thermotropic hexagonal columnar (Φ_h) LC phase.

Experimental Section

Materials. $Pd^0[PPh_3]_4$ was prepared according to a literature procedure.[21] 1,5-Hexadiene (98%), 1,7-octadiene (98%), and 1,9-decadiene (98%, all from Aldrich) were distilled from $NaBH_4$ prior to use. 1,4-Diiodoperfluorobutane (97%) and 1,6-diiodoperfluorohexane (97%, both from PCR) were washed with 5% $Na_2S_2O_3$, dried over $MgSO_4$, and filtered prior to use. 1,10-Diiodoperfluorodecane (PCR) and Bu_3SnH (97%, Aldrich) were used as received. Toluene was washed with H_2SO_4 until the washes were colorless and then washed with H_2O, dried over $MgSO_4$, filtered, and distilled from sodium benzophenone ketyl under N_2. 2,2′-Azobis[isobutyronitrile] (AIBN) was recrystallized from MeOH at 4 °C. Silica gel, 1,1,2-trichlorotrifluoroethane (both from Fisher), and other conventional reagents were used as received.

Methods. ^1H, ^{19}F (200, 188 MHz respectively) NMR spectra were recorded on a Varian Gemini 200 at 20 °C (except as indicated), with tetramethylsilane (TMS) internal standard for ^1H and fluorotrichloromethane ($CFCl_3$) internal standard for ^{19}F. Relative molecular weights of polymers were measured by gel permeation chromatography (GPC) with a Perkin-Elmer Series 10 LC pump, equipped with an LC-100 column oven (40 °C), a UV detector, and Nelson PC Integrator software. A set of two Polymer Laboratories PL gel columns of 5×10^2 and 10^4 Å and THF eluent at 1 mL min^{-1} was used. Polystyrene standards were used for calibration. Differential scanning calorimetry (DSC) measurements were recorded on a Perkin-Elmer DSC-7. Indium and zinc were used as calibration standards. Heating and cooling rates were 10 °C min^{-1}. First-order transitions are reported as the maximum of endothermic and minimum of exothermic peaks. Glass transitions were calculated as the middle of the change in heat capacity. An Olympus BX-40 optical polarized microscope (100× magnification) equipped with a Mettler FP 82 hot stage and a Mettler FP 80 central processor was used to verify thermal transitions and characterize anisotropic textures. X-ray scattering patterns were recorded by using either a helium-filled flat-plate wide-angle (WAXS) camera or a pinhole-collimated small-angle (SAXS) camera, and also by using an image plate area detector (MAR Research) with a graphite-monochromatized pinhole-collimated beam and a helium tent. The samples, in glass capillaries, were held in a temperature-controlled cell (±0.1 °C). Ni-filtered Cu Kα radiation was used.

Synthesis of 3-*X/Y/Z(A/B/C)-x/y/z(a/b/c)*. Method A: 3-*6/8/10(33/33/33)-4/6/10(29/29/29)*. A 25 mL Schlenk tube containing a Teflon-coated magnetic stirring bar was charged with 0.439 g (0.966 mmol) of 1,4-diiodoperfluorobutane, 0.547 g (0.988 mmol) of 1,6-diiodoperfluorohexane, 0.722 g (0.958 mmol) of 1,10-diiodoperfluorodecane, 0.093 g (1.1 mmol) of 1,5-hexadiene, 0.124 g (1.1 mmol) of 1,7-octadiene, and 0.152 g (1.1 mmol) of 1,9-decadiene. The mixture was subjected to five freeze−pump−thaw cycles. $Pd[PPh_3]_4$ was added in two 0.07 g (0.07 mmol) portions, and the mixture was stirred at room temperature until the increase in viscosity caused the stirring to stop (<30 min). The polymer was dissolved in 2 mL of THF and precipitated into 70 mL of MeOH. The crude polymer was then dissolved in 10:1 hexanes/THF and chromatographed on silica gel using a gradient eluent (hexanes to hexanes/THF 100:1) to yield 1.2 g (57%) of a slightly yellow gummy solid. GPC: M_n = 7300, M_w/M_n = 1.8. ^1H NMR ($CDCl_3$, TMS, ppm): δ 1.26−2.20 (m, CH_2), 2.59−3.10 (m, CF_2CH_2CHI), 4.34 (m, CF_2CH_2CHI), 4.90−5.18 (m, CH_2=CH), 5.65−5.91 (m, CH_2=C*H*). ^{19}F NMR ($CDCl_3$, $CFCl_3$, ppm): δ −113.70 (q, CF_2CH_2CHI, J_{F-H} = 266.4 Hz), −122.27 (s, $CF_2CF_2CF_2CH_2$), −124.12 (s, $CF_2CF_2CH_2$).

Method B: 3-*10/0/0(100/0/0)-4/6/0(50/50/0)*. This polymerization was carried out according to a literature procedure.[10] A 25 mL Schlenk tube containing a Teflon-coated magnetic stirring bar was charged with 0.626 g (1.12 mmol) of 1,6-diiodoperfluorohexane, 0.508 g (1.12 mmol) of 1,4-diiodoperfluorobutane, and 0.310 g (2.24 mmol) of 1,9-decadiene. The mixture was subjected to five freeze−pump−thaw cycles and placed in an 80 °C oil bath, and 0.295 g (1.80 mmol) of AIBN was added in 0.024 g portions over 3 h. The oil bath temperature was gradually increased to 135 °C during this period. A cold finger was inserted into the Schlenk tube, and the residual AIBN as well as its decomposition products was sublimed under vacuum. The resulting polymer was then dried overnight at 90 °C under vacuum, yielding 1.4 g (93%) of an orange viscous liquid. GPC: M_n = 10 300, M_w/M_n = 2.3. ^1H NMR ($CDCl_3$, TMS, ppm): δ 1.26−2.20 (m, CH_2), 2.59−3.10 (m, CF_2CH_2CHI), 4.34 (m, CF_2CH_2CHI), 4.90−5.18 (m,

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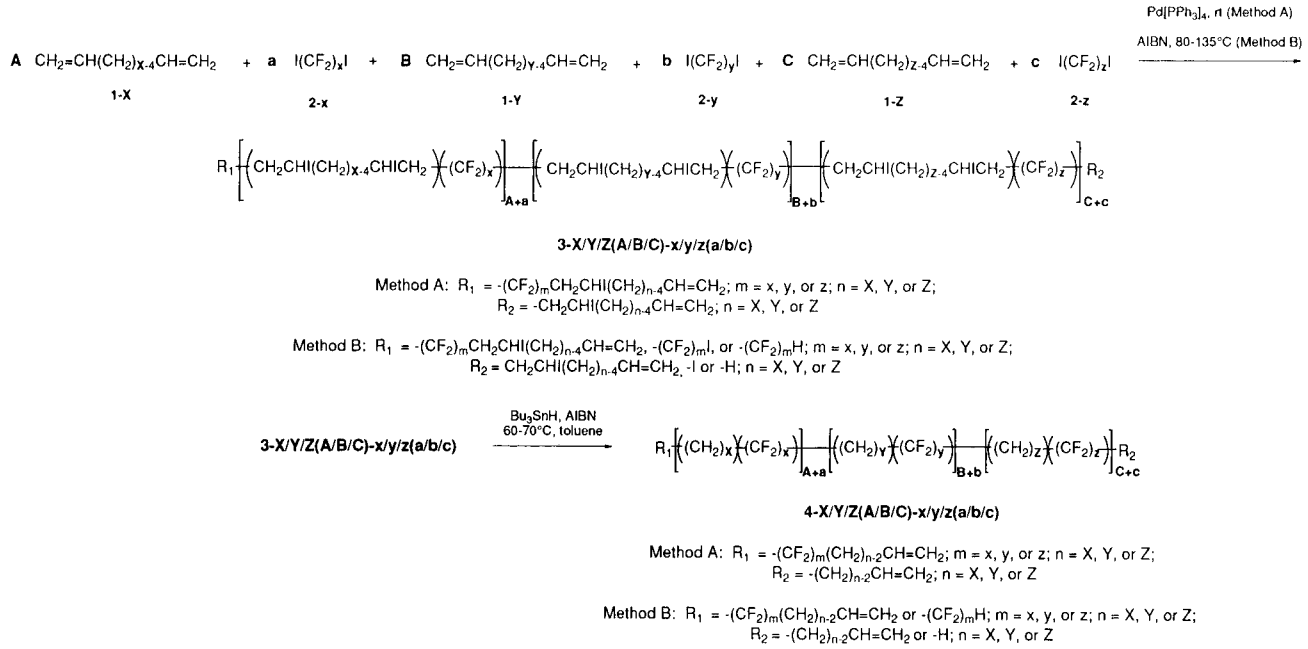
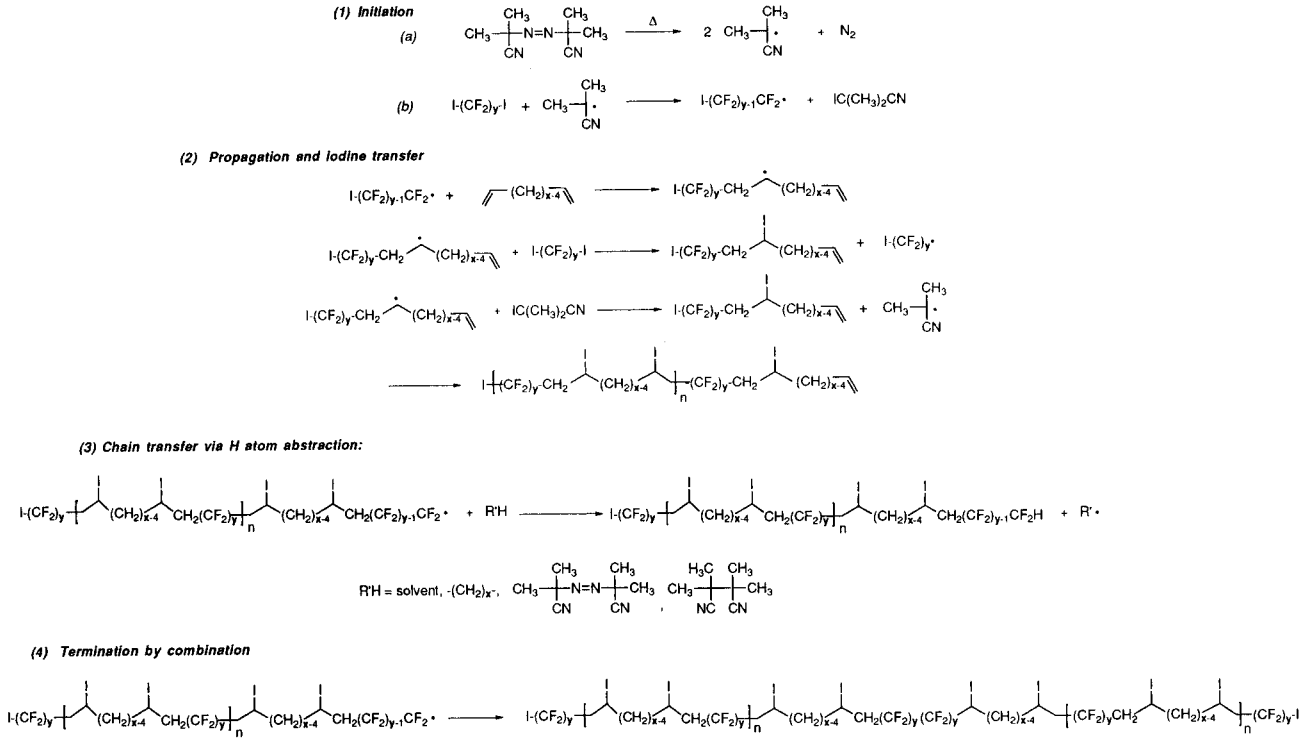
Scheme 1. Synthesis of Olefin-Terminated Semifluorinated Polyethylenes



Scheme 2. Mechanism of Conventional AIBN-Initiated Radical Polymerization of α,ω-Diiodoperfluoroalkanes with α,ω-Dienes



CH_2═CH), 5.65−5.91 (m, CH_2═C*H*). ^{19}F NMR ($CDCl_3$, $CFCl_3$, ppm): δ −59.2 (CF_2I), −113.7 (q, CF_2CH_2CHI, J_{F-H} = 266.4 Hz), −122.27 (s, $CF_2CF_2CF_2CH_2$), −124.1 (s, $CF_2CF_2CH_2$), −126.1 (s, $CF_2CF_2CF_2H$), −130.1 (s, CF_2CF_2H), −137.5 (m, CF_2H).

Reduction of Iodide Groups of Precursor Polymers, 4-*X/Y/Z(A/B/C)-x/y/z(a/b/c)*: 4-*6/8/10(33/33/33)-4/6/10(29/29/29)*. A 50 mL three-neck round-bottom flask containing a Teflon stir bar was charged with 0.92 g of polymer dissolved in 10 mL of toluene and 13 mg (0.078 mmol) of AIBN. The flask was flushed with Ar and closed with a rubber septum, glass stopper, and Ar inlet−outlet. The solution was heated to 60 °C, and Bu_3SnH (0.80 mL, 2.9 mmol) was added dropwise *via* syringe over a 45 min period. The reaction temperature was increased to 70 °C, stirred for 3 h, and then cooled to room temperature. ^{1}H NMR indicated complete reduction of iodide groups. The solution was precipitated into MeOH. The resultant solid was filtered, washed with MeOH, and then redissolved in either warm $CHCl_3$ or THF and precipitated into MeOH. This procedure was repeated two times to yield 0.543 g (78.7%) of gray solid. ^{1}H NMR ($CDCl_3$, 50 °C, TMS, ppm): δ 1.26−1.72 (overlapped, CH_2), 1.91−2.23 (m, CF_2CH_2), 4.90−5.18 (m, CH_2═CH), 5.65−5.91 (m, CH_2═C*H*). ^{19}F NMR ($CDCl_3$, 50 °C, $CFCl_3$, ppm): δ −114.8 (s, CF_2CH_2), −122.3 (s, $CF_2CF_2CH_2$), −124.2 [$(CF_2)_xCF_2CF_2CH_2$].

Results and Discussion

Scheme 1 outlines the conventional AIBN-initiated polymerization of α,ω-diiodoperfluoroalkanes with α,ω-dienes,[10] which is based on Brace's classic organic

Table 1. Characterization of 3-*X/Y/Z(A/B/C)-x/y/z(a/b/c)* Obtained by AIBN-Initiated Radical Polymerization and Pd(0) Single-Electron Transfer (SET) Radical Polymerization of Various α,ω-Dienes with α,ω-Diiodoperfluoroalkanes

entry	initiator	$[M]_0/[I]_0$	*X/Y/Z(A/B/C)*	*x/y/z(a/b/c)*	reaction conditions	yield (%)[a]	M_n (GPC)	M_w/M_n (GPC)	DP(*n*) (GPC)	M_n (NMR)
1	AIBN	100	8/0/0(100/0/0)	4/0/0(100/0/0)	60 °C, 12 h	8	1500	1.6	4	
2	AIBN	0.83	10/0/0(100/0/0)	4/0/0(100/0/0)	80−120 °C, 3 h	96	15100	2.7	40	
3	$Pd[PPh_3]_4$	40	10/0/0(100/0/0)	4/0/0(100/0/0)	0 °C to rt, 5 min	59	5200	1.9	17	
4	$Pd[PPh_3]_4$	40	6/8/0(50/50/0)	6/0/0(100/0/0)	rt, 5 min	64	5900	1.9	18	4100
5	$Pd[PPh_3]_4$	10	10/0/0(100/0/0)	4/0/0(100/0/0)	80−120 °C, 3 h	*b*	*b*	*b*	*b*	*b*
6	$Pd[PPh_3]_4$	91	6/8/10(33/33/33)	4/6/0(43/43/0)	rt, 30 min	73	2200	2.2	4	3100
7	$Pd[PPh_3]_4$	48	6/8/10(33/33/33)	4/6/10(29/29/29)	rt, 30 min	57	7300	1.8	14	5700
8	$Pd[PPh_3]_4$	39	10/0/0(100/0/0)	4/0/0(100/0/0)	rt, 3 h, hexanes	65	5200	2.1	17	
9	$Pd[PPh_3]_4$	40	6/8(50/50/0)	4/0/0(87/0/0)	rt, 5 min	62	2600	1.6	5	2300
10	$Pd[PPh_3]_4$	39	8/0/0(100/0/0)	6/0/0(100/0/0)	rt, 5 min, THF	56	5900	2.0	18	

[a] Isolated yield. [b] Insoluble product.

Table 2. Thermal Characterization of Polymers 4-*X/Y/Z(A/B/C)-x/y/z(a/b/c)* by Differential Scanning Calorimetry (DSC, Data from the First Heating Scan on the First Line, and Data from the Second Heating Scan on the Second Line) and X-ray Scattering Experiments (100 Spacing and Column Diameter (*D*, Å) at Various Temperatures) of the Hexagonal Columnar (Φ_h) Mesophase

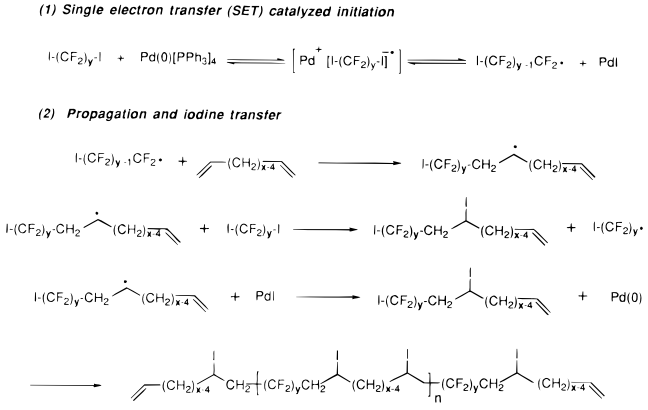
			thermal transitions (°C) and corresponding enthalpy changes (kcal/mru) in parentheses		characterization of the Φ_h phase by X-ray diffraction experiments		
entry	*X/Y/Z(A/B/C)*	*x/y/z(a/b/c)*	heating	cooling	temp (°C)	d_{100} (Å)	*D* (Å)[b]
1	6/8/10(33/33/33)	4/6/10(29/29/29)	Φ_h 132, 139, 155 (6.23)[a] i	i 146 (6.41) Φ_h	32	4.615	5.329
			Φ_h 152 (6.41) i		50	4.635	5.352
					70	4.655	5.375
					90	4.685	5.410
					110	4.701	5.428
					130	4.739	5.472
2	8/0/0(100/0/0)	4/6/0(43/43/0)	Φ_h 126, 140, 158 (5.68)[a] i	i 150 (5.55) Φ_h	45	4.586	5.295
			Φ_h 155 (5.58) i		100	4.658	5.379

[a] Combined enthalpy. [b] $D = 2(d_{100})/3^{1/2}$.

reaction[22] and the Pd(0) single electron transfer (SET) reaction. The SET reaction[23] was successfully used in our laboratory for the synthesis of a large variety of functional semifluorinated building blocks which required very mild reaction conditions.[13,18−20] Both reactions are performed in bulk. The second step in both reaction procedures consists of the quantitative reduction of iodide groups with Bu_3SnH.[10,24]

Scheme 2 outlines the mechanism of the AIBN-initiated polymerization reaction (method B). This reaction is initiated at 80 °C and requires a high polymerization temperature to produce high conversions. Since the source of radicals (AIBN) is consumed, this polymerization requires a high concentration of initiator. Due to the inability to control the concentration of radicals under these conditions, besides initiation, propagation, iodine transfer, and termination, the undesired chain transfer *via* H-abstraction takes place. The SET Pd(0)-catalyzed reaction (method A) is carried out at room temperature, under very mild reaction conditions, and with an extremely small concentration of radicals which are in dynamic equilibrium with their covalent iodide species. The concentration of radicals in the SET polymerization is controlled by the concentration of the Pd(0) catalyst. By analogy with "living" radical polymerizations initiated *via* related metal-catalyzed processes,[25] chain transfer *via* H-abstraction is not observed in this polymerization (Scheme 3). In addition, the SET-catalyzed polymerization can be performed either in bulk or in solution. Therefore, a stoichiometric imbalance between the two monomers yields polymers with controlled chain ends. A combination of ^1H and ^{19}F spectroscopies was used for the characterization of the polymers obtained by both synthetic methods. Figure 1 presents ^{19}F NMR spectra of selected polymers obtained by SET (method A, spectrum a) and AIBN (method B, spectra b and c)

Scheme 3. Mechanism of Pd(0)-Initiated Single Electron Transfer (SET) Polymerization of α,ω-Diiodoperfluoroalkanes with α,ω-Dienes



methods (assignments are given in the figure), which support the mechanisms outlined in Schemes 2 and 3 and the structure from the top of each spectrum. The olefinic chain ends of these telechelic polymers can be functionalized further *via* conventional organic reactions. Table 1 lists the characterization data of **3**-*X/Y/Z(A/B/C)-x/y/z(a/b/c)*.

Chart 1 depicts the formation of the lamellar S_B phase in binary alternating copolymers and of the Φ_h mesophase in multiblock alternating copolymers generated from dissimilar repeat units.[26] Increasing the number of the repeat units of the binary alternating copolymer to more than two *via* changing the length of at least one of the two monomers breaks the ability to register fluorinated and hydrogenated blocks into individual layers to form the lamellar S_B phase and consequently yields a Φ_h phase. This synthetic technique was developed and used extensively in our laboratory to generate a Φ_h mesophase in main-chain LC copolymers.[26] This

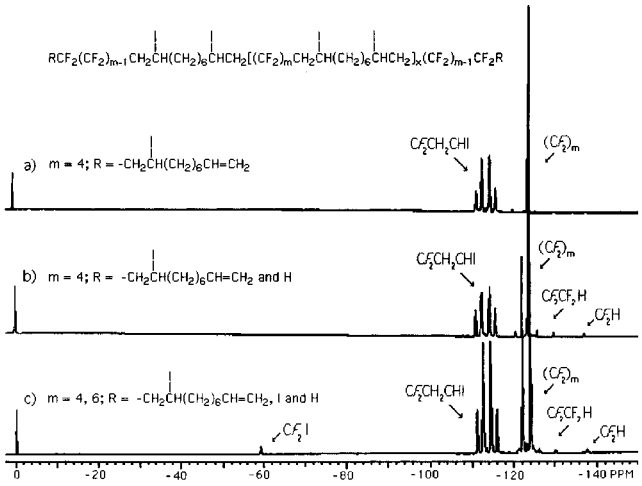
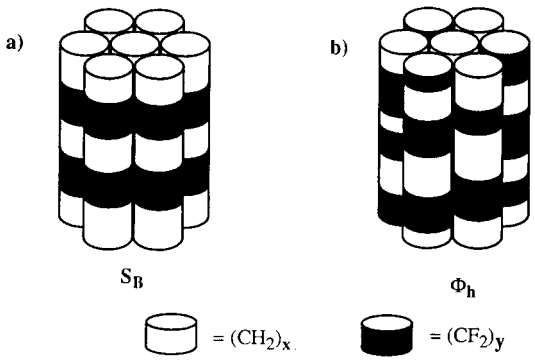


Figure 1. (a) Representative ^{19}F NMR spectrum of **3**-*10/0/0(100/0/0)-4/0/0(87/0/0)* obtained by $Pd[PPh_3]_4$-initiated polymerization (method A) of 1,9-decadiene with 1,4-diiodoperfluorobutane using an excess of 1,9-decadiene; (b) Representative ^{19}F NMR spectrum of **3**-*10/0/0(100/0/0)-4/0/0(87/0/0)* synthesized by AIBN-initiated polymerization (method B) of 1,9-decadiene with 1,4-diiodoperfluorobutane using an excess of 1,9-decadiene. (c) Representative ^{19}F NMR spectrum of **3**-*10/0/0(100/0/0)-4/6/0(50/50/0)* obtained by AIBN-initiated polymerization (method B) using a 1:1 molar ratio of 1,9-decadiene and 1,4-diiodoperfluorobutane, and 1,6-diiodoperfluorohexane.

Chart 1. Schematic Representation of (a) the S_B Phase of 4-*6/0/0(100/0/0)-6/0/0(100/0/0)* Copolymer and (b) the Hexagonal Columnar (Φ_h) Phase of 4-*6/8/10(33/33/33)-4/6/10(29/29/29)*



series of experiments has demonstrated the application of this strategy to semifluorinated paraffins. Increasing the number of repeat units from two to three, five, and, respectively, six dissimilar perfluorinated and perhydrogenated segment lengths transforms the S_B phase of the parent binary alternating copolymer to a Φ_h LC phase. The Φ_h phase of these polymers was characterized by a combination of techniques consisting of DSC, X-ray diffraction, and thermal optical polarized microscopy (fan shape texture with homeotropic domains). Table 2 summarizes the characterization data for selected examples of semifluorinated polyethylenes. More detailed investigations of the physical properties of these polymers are in progress and will be presented elsewhere.

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