Liquid-Crystalline Behavior in a Series of Fluorocarbon Side-Chain Polyesters. 2

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ABSTRACT: A series of liquid-crystalline polyesters has been synthesized in which the mesogenic perfluoroalkylsulfonyl sidechain is directly linked to the hydrocarbon polyester backbone without a spacer. The liquid-crystalline phase appears to be smectic B or A from X-ray data. Interesting differences in the mesophase transition temperatures and enthalpies are observed along the series, as the hydrocarbon backbone is changed. Differences are also seen in layer spacing from X-ray data, which increases as the hydrocarbon content increases. We discuss these in relation to the length of the backbone segments.

Introduction

The liquid-crystalline (LC) behavior of a series fluorocarbon side-chain polyesters of the type[1]

$$[-OCH_2CH_2N(SO_2(CF_2)_8F)CH_2CH_2O_2CR_mCO-]_n$$

with $m = 2$–10 inclusive and $m = 12$ and 20 has been investigated. Some physical properties such as surface energies have also been measured. Two series of side-chain liquid crystal polymers having spacing along the main chain greater than a single methylene (as in the acrylate type systems) are known, based on the polysiloxane backbone with pendant aromatic mesogens[2] or with fluorinated or semifluorinated mesogens as side groups.[11] However, we believe that the polyesters described here are the first fluorinated polymers of this type to show liquid-crystalline behavior. Unlike the polyacrylate systems with perfluoroalkyl side chains,[4] these polyesters show liquid-crystalline mesophases without having flexible $-(CH_2)-$ spacer linkages from the fluoroalkyl to the polymer backbone.

The relative magnitudes of the enthalpies in the DSC change on going along the series. The enthalpy of the lower temperature (solid to mesophase) transition becomes greater than the upper at $m = 4$ and increases with m, while the minimum in both enthalpies is at $m = 5$. The polymers with $m > 3$ have LC mesophases. It was found that the mesophase to isotropic transition temperatures also change along the series and have an odd–even effect in the value of m. The molar enthalpies for the mesophase transitions in most of the polymers were found to be unexpectedly high, reminiscent of segregated materials.

The polyacrylate systems having fluorocarbon–hydrocarbon side-chains have previously been investigated and show highly ordered smectic B mesophases.[3,4] The polyesters described here also show a fluid smectic mesophase which appears to be smectic B (by analogy with the polyacrylates) or smectic A from X-ray diffraction data. The phase has a grainy texture in the polarizing microscope, which becomes larger on annealing and has areas of blue and gold coloration. These polyesters can be sheared easily in the mesophase temperature range.[1]

Experimental Section and Polymer Characterization

All polymers were prepared as described in ref 1 and characterized by NMR (in $CDCl_3$), elemental analysis, GPC (in $CHCl_3$), and IR. Elemental analyses and NMR characterization data for the polymers are shown in Table 1.

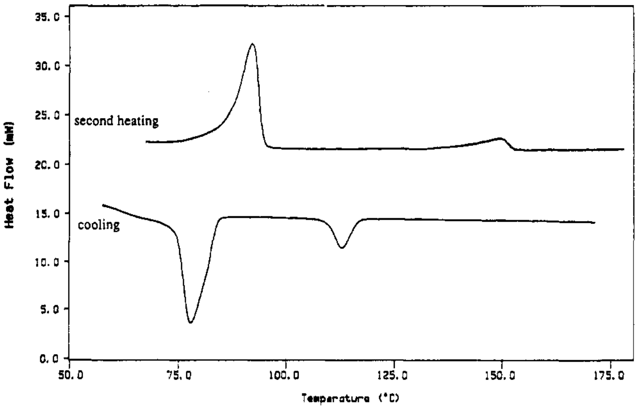

Figure 1. DSC plot for polyester with $m = 12$, showing second heating and cooling, run at 10 °C/min.

In the IR all showed a fluoroalkyl at 1290–1060 cm^{-1} (strong), an ester at 1737 cm^{-1}, and a hydrocarbon at 3000–2850 cm^{-1}.

$\bar{M}_n$ by GPC in $CHCl_3$ was 12–40 000 in all cases (polystyrene standards). Measurements were performed on the following instruments: IR on a Nicolet 510M spectrometer; NMR on a Bruker WM250 MHz spectrometer; GPC on a Polymer Laboratories–Knauer system with RI and UV detectors; DSC on a Perkin-Elmer Series 7 and Du Pont 2100; polarizing light microscopy on a Leica axioscope fitted with a Mettler FP82 microfurnace. Elemental analyses were performed in the Department of Chemistry, University of Cambridge; surface energies were measured in the Department of Physics, University of Cambridge, on a Kreuss processor tensiometer K12, V3.11.

The small-angle X-ray diffraction measurements were performed on a Philips PW 1710 diffraction system.

The samples were prepared by heating to the isotropic phase and cooling down into the mesophase or annealing at the mid-mesophase temperature for several minutes. The samples were then quenched in liquid nitrogen and ground to powders for the X-ray measurements.

Results and Discussion

The DSC traces show fairly large and clear transitions and an example is shown in Figure 1. Solid to mesophase and mesophase to isotropic-liquid transition temperatures are shown in Table 2 and plotted in Figure 2, vs m, the number of methylene units in the hydrocarbon comonomer of the polyester backbone. These values have been checked on the microscope hot stage, and all the polymers showing a mesophase could be easily sheared in the mesophase temperature range, which has also been shown previously by dynamic mechanical analysis over the mesophase

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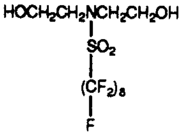
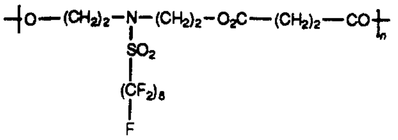
Table 1. Chemical Analysis Data for Fluorinated Monomer and Polyesters

compound elem anal.			^{1}H NMR (δ) (in CDCl$_3$ unless shown otherwise) (in ppm vs TMS)
	calc	found	
 $HOCH_2CH_2N(SO_2(CF_2)_8F)CH_2CH_2OH$			in (CD$_3$)$_2$CO 4.35 (t, 1H) 3.83 (t, 2H) 3.75 (m, 1H) 3.64 (m, 1H)
H	1.70	1.64	
C	24.50	24.54	
N	2.39	2.43	
 $-\!\!\left[O-(CH_2)_2-N(SO_2(CF_2)_8F)-(CH_2)_2-O_2C-(CH_2)_2-CO\right]_n$			
polymer with $m = 2$			
H	1.79	1.89	4.42 (m, 2H)
C	28.70	29.02	3.94 (m, 1H)
N	2.09	2.13	3.74 (m, 1H)
			3.77 (s, 2H)
polymer with $m = 3$			
H	2.05	2.11	4.30 (m, 2H)
C	29.87	30.02	3.84 (m, 1H)
N	2.05	2.04	2.61 (m, 1H)
			2.41 (s, 2H)
			1.97 (m, 1H)
polymer with $m = 4$			
H	2.29	2.26	4.28 (t, 2H)
C	31.00	31.24	3.83 (m, 1H)
N	2.01	1.94	3.62 (m, 1H)
			2.36 (t, 2H)
			1.65 (m, 2H)
polymer with $m = 5$			
H	2.53	2.56	4.28 (t, 2H)
C	32.07	31.98	3.81 (m, 1H)
N	1.97	1.94	3.64 (m, 1H)
			2.33 (t, 2H)
			1.64 (m, 2H)
			1.34 (m, 1H)
polymer with $m = 6$			
H	2.76	2.78	4.30 (t, 2H)
C	33.10	33.26	3.81 (m, 1H)
N	1.93	1.90	3.65 (m, 1H)
			2.32 (t, 2H)
			1.58 (m, 2H)
			1.32 (m, 2H)
compound elem anal.	calc	found	^{1}H NMR (δ) (in CDCl$_3$) (in ppm vs TMS)
polymer with $m = 7$			
H	2.98	3.01	4.30 (t, 2H)
C	34.10	34.15	3.81 (m, 1H)
N	1.89	1.88	3.64 (m, 1H)
			2.33 (t, 2H)
			1.59 (m, 2H)
			1.32 (m, 3H)
polymer with $m = 8$			
H	3.19	3.20	4.31 (t, 2H)
C	35.06	35.28	3.84 (m, 1H)
N	1.86	1.83	3.65 (m, 1H)
			2.35 (t, 2H)
			1.62 (m, 2H)
			1.32 (m, 4H)
polymer with $m = 9$			
H	3.39	3.26	4.30 (t, 2H)
C	35.98	36.00	3.83 (m, 1H)
N	1.82	1.75	3.65 (m, 1H)
			2.33 (t, 2H)
			1.60 (m, 2H)
			1.31 (m, 5H)
polymer with $m = 10$			
H	3.58	3.55	4.28 (t, 2H)
C	36.87	37.12	3.83 (m, 1H)
N	1.79	1.76	3.65 (m, 1H)
			2.33 (t, 2H)
			1.60 (m, 2H)
			1.28 (m, 6H)
polymer with $m = 12$			
H	3.95	3.96	4.26 (t, 2H)
C	38.60	38.65	3.85 (m, 1H)
N	1.73	1.70	3.66 (m, 1H)
			2.33 (t, 2H)
			1.61 (m, 2H)
			1.25 (m, 8H)
polymer with $m = 20$			
H	5.21	5.24	4.28 (t, 2H)
C	44.30	44.20	3.83 (m, 1H)
N	1.52	1.56	3.64 (m, 1H)
			2.31 (t, 2H)
			1.60 (m, 2H)
			1.23 (m, 16H)

temperature range.[1] The polyesters with $m > 3$ have a thermotropic liquid-crystalline phase. The solid to mesophase temperatures show a wide variation along the series as m is increased, showing a rapid decrease and then increasing more slowly for higher m. This is similar to the behavior seen in LC side-chain polymers with flexible spacer units.[5] The upper mesophase to isotropic temperatures also show a drop to a minimum and then appear to flatten out, but there is a pronounced odd–even effect of the m values in the backbone, with the even values having higher transition temperatures. If genuine and not an artefact of molecular weight variation or other factors, this is unexpected for a side-chain LC polymer, and since the fluorinated diol monomer itself has an odd number of atoms along the backbone of the polymer, it might not be clear why the effect is seen with the even values of m having higher transition temperatures.

One explanation might be that this effect is analogous to the odd–even effect in main-chain aliphatic polyesters[6] and in main-chain liquid-crystalline materials with aliphatic spacers,[7] where the value of m in the spacer has a large effect on the ordering of the mesogens, and that here the hydrocarbon diester groups along the backbone in fact are bent as "hairpins", with the rigid fluorocarbon at the angle of the bend. The hairpin is then acting as a normal flexible "spacer" as in other side-chain LC polymers. The odd value of m may then disrupt the order more than even values. It is clear from the LC behavior that the flexible hydrocarbon backbone itself can act as a mesogen spacer, in decoupling and/or lowering the melting point of the polymers sufficiently to give an observable mesophase. The minimum in the transition temperature was at $m = 5$. In fact many main-chain and side-chain (m in the spacer) systems show a minimum at this value of m. While only the two upper (higher temperature) transitions are listed in Table 2, most of the polyesters show a lower temperature endotherm transition at about 35–55 °C, which is associated with a first-order solid–solid transition. However, the polyesters with $m = 3$ and 4 do soften at this transition, and the polyester with $m = 4$ shows some texture in the polarizing optical microscope between 55 and 76 °C, so the transitions listed are the solid or soft solid to mesophase and the clearing transitions.

The molecular ordering or phase separation in these polymers may be analogous to the polysiloxane systems mentioned in the Introduction.[4,11] If it is true that the

Table 2. Thermal Transition Temperatures and Transition Enthalpies from DSC for Mesomorphic Polyesters Having Different *m*

	solid–mesophase			mesophase–isotropic		
m	temp (°C)	enthalpy (J/g)	enthalpy (kJ/mol repeat unit[c])	temp (°C)	enthalpy (J/g)	enthalpy (kJ/mol repeat unit[c])
0[a]	112[a]	23	13.5	158[a]	14.5	8.5
2[b]	125[b]	8.25	5.5	160[b]	10.5	7.0
3[b]	111[b]	2.5	1.7	150[b]	13	8.9
4	76	10	7.0	145	5	3.5
5	60	1.0	0.71	108	0.25	0.18
6	75.5	4.0	2.9	149.7	2.7	1.9
7	76.5	10.3	7.6	131	7.2	5.3
8	87	19	14.3	150	8.8	6.6
9	83	19.5	14.9	134.7	8.1	6.2
10	87	27.1	21.2	156.5	11.64	9.1
12	91	36.5	29.5	148	10.7	8.6
20	97	49	45.1	152	8.25	7.6

[a] Perfluoroalkyldiol monomer compound. [b] These polymers do not have fluid mesophases. [c] Calculated for mole equivalent of the monomer–comonomer repeat unit of the polymer chain.

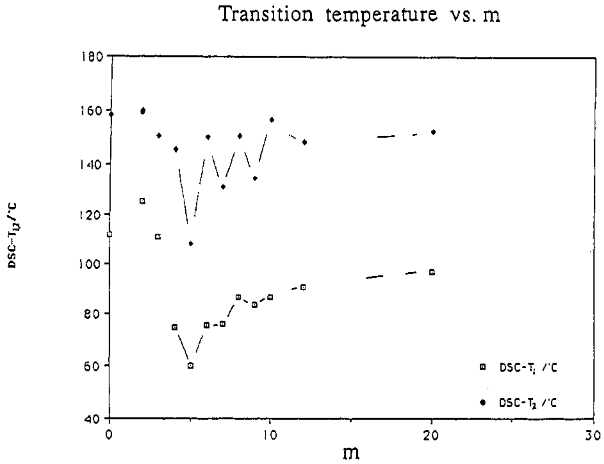


Figure 2. DSC transition temperatures, solid to mesophase (T_1) and mesophase to isotropic (T_2) vs *m*, for fluorinated polyesters.

aliphatic backbone chain flexibility allows ordering and segregation in these polyesters, then by analogy it can be predicted that a polysiloxane having similar perfluoroalkyl side chains without any flexible spacer groups (to the side chains) would be liquid crystalline and perhaps also other systems with long hydrocarbon spacing along the backbone between pendant (fluoroalkyl or other) mesogens.

On cooling in the DSC there is considerable undercooling of the upper clearing transition, of 30–45 °C at a rate of 10 °C/min and 25–38 °C at 5 °C/min, suggesting the process of ordering is kinetically sluggish, compared to the fluorocarbon–hydrocarbon main chain polymers[8] which only show ~3–7 °C undercooling in both transitions at 5 °C/min. This may be expected if the system is going to a highly ordered phase such as smectic B from the isotropic melt. The lower transition shows much less undercooling, ~3–16 °C at 5 or 10 °C/min.

The enthalpies of the upper and lower transitions also change, as mentioned in the Introduction. The relative magnitudes cross over at *m* = 4, which is the first member of the series to show a fluid mesophase, with the lower transition enthalpy becoming greater than the clearing point enthalpy. These are shown in Table 2 and plotted vs *m* in Figure 3. The magnitude of both shows a minimum at *m* = 5. This value of *m* also corresponds to the minimum value of the transition temperature (Figure 2) and suggests that with five methylene units there is a maximum disruption to the ordering of the fluorocarbon rods as well as the backbone. There is no convincing odd–even effect of *m* in the values of the upper transition enthalpy (Figure 3) reflecting this disruption and the temperature variation in Figure 2. The increasing values of the enthalpy for the lower temperature transition as *m* increases reflect the increasing proportion of hydrocarbon in the polymer. This supports the view that the lower transition is due to the hydrocarbon, as does the observation that the upper transition enthalpy (J/g) does not increase above its maximum value but finally begins to decline when measured in J/g as the proportion of fluorocarbon in the polymers decreases with increasing *m* (Table 2). But when calculated in kJ/(mol equiv of polymer repeat unit), it shows a fairly flat plateau of values (except for the sharp decrease at around *m* = 5), with the upper level value being 9 kJ/(mol of repeat unit). This represents the enthalpy of disruption of the perfluoroalkyl side chains and is shown in Figure 3. Previously, evidence for the assignment of these two transitions was found by comparison with hydrocarbon polyesters.[1]

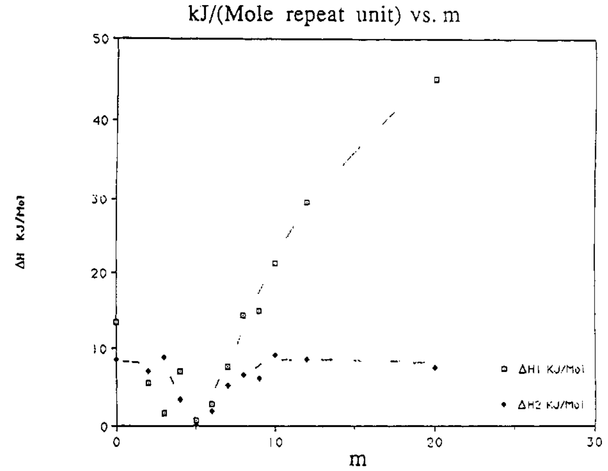


Figure 3. Transition enthalpies in kJ/(mol of repeat unit) vs *m*, for fluorinated polyesters: solid to mesophase (ΔH_1) and mesophase to isotropic (ΔH_2).

Powder X-ray diffraction measurements were made to investigate the liquid-crystalline mesophase structure on quenched samples. The resulting patterns are relatively simple and informative. The Bragg *d* spacings and the intensity versus angle diagrams are shown in Figure 4 for the fluorinated side-chain polyesters with *m* = 6, 12, and 20. They show strong sharp peaks at low angles and peaks at high angles. The ratios of the spacings corresponding to the sharp low-angle peaks are $1:{}^1/_2:{}^1/_3$, indicating 001, 002, and 003 indexing due to periodic layer spacings in a smectic phase. At high angle there is one main peak which is rather narrow (but broader than the low-angle peaks). This suggests an arrangement with a fairly good orientation correlation, and thus the ordering in the layers may be a smectic B phase (for lower *m*) or perhaps a smectic A type phase. From molecular models the side-chain length with the hydrocarbon (in a folded hairpin arrangement) to give smectic layers can be calculated, and for *m* = 6 it is approximately 21 Å. The X-ray diffraction data show the layer periodicity (001 index) is nearly 33 Å and the ratio of the observed (*d*) to the calculated (*L*) lengths is 1.59, showing there is bilayer ordering in this mesophase. This is similar to the *d* spacing for the polyacrylate (having a single methylene between side groups along the polymer backbone) with the side-chain units $F(CF_2)_8CH_2CH_2O_2C$– found by Shimizu[10] in which the spacing was found to be 33 Å. In this polyacrylate the repeat unit length was about 17 Å, indicating a bilayer which is not tilted or interpenetrated. However, with the polyesters described here there is a longer hydrocarbon chain (of *m* methylenes in the comonomer) between each side group along the backbone and the bilayer is highly tilted or quite interpenetrated.

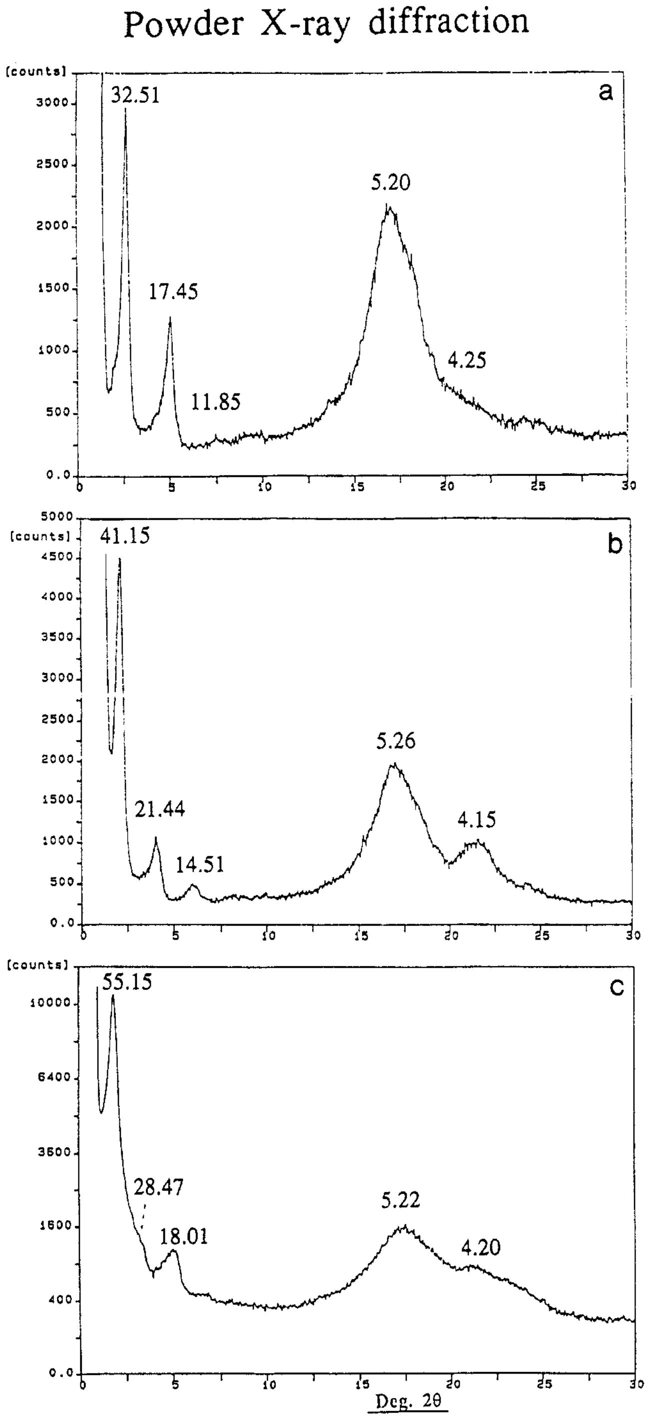


Figure 4. Powder X-ray diffraction plots for fluorinated polyesters with $m = 6$ (a), 12 (b), and 20 (c) showing d spacings in angstroms.

The greater chain length between side groups presumably could allow overlap of the perfluorocarbons, giving a bilayer spacing which is less than twice the repeat length (L), perhaps similar to antiparallel dimer packing of some smectics. For the polyester with $m = 12$, the layer thickness is calculated to be approximately 25 Å. The X-ray data show a layer periodicity of 41.15 Å, giving a ratio (d/L) of 1.68. For $m = 20$ the layer thickness is calculated to be approximately 30 Å. The X-ray data show a layer periodicity of 55 Å, again showing a bilayer arrangement with a ratio (d/L) of 1.83.

At large angle there is a peak corresponding to 5.2 Å in the polymer with $m = 6$. With $m = 12$ and 20 this peak is also dominant. This spacing corresponds to the expected lateral distance between perfluoroalkyl chains. When $m = 12$, there is a second smaller peak corresponding to 4.25 Å, and also in the polymer with $m = 20$, there is a broad peak at this angle. In fact the first polymer ($m = 6$) also has a small shoulder at this position. The appearance of this peak which becomes more prominent on going from $m = 6$ to 20 (and the increasing broadness of the main peak) may indicate a move away from a possible hexagonal smectic B ordering to some other arrangement in the layers of the smectic phase such as smectic A. Howevr, since the textures in the microscope between crossed polarizers are all similar and this spacing corresponds to the lateral distance between hydrocarbon chains, it is likely that this is in fact the lateral hydrocarbon chain spacing between nearest neighbors and grows in importance as the proportion of hydrocarbon in the polyester increases. This hydrocarbon spacing is often seen in organic compounds. The fact that both the perfluorocarbon and hydrocarbon lateral nearest-neighbor spacings can be observed also supports a smectic A mesophase.

Table 3. Surface Energies of Fluorinated Polyesters (erg/cm^2)

m	% fluorine in polymer	surface energy (erg cm^{-2})[a]
4	46.3	15.5
8	42.9	16.5
12	39.9	18
20	35	18.5
PTFE	76.0	19.1

[a] Average of three measurements.

In these polymers we see the layer periodicity increases as the number of methylene units (m) in the polymer increases, while the relative intensities of the high-angle spacing (5.2 and 4.25 Å) due to the perfluoroalkyl and the hydrocarbons chains also change.

Some surface energies shown in Table 3. The values of surface energies are comparable with PTFE or lower, even with fluorine contents as low as 24% by weight[9] for a terpolymer with other hydrocarbon comonomers. The polyesters are liquid crystalline, with smectic mesophases probably having interpenetrated bilayer arrangements of the perfluoroalkyl side chains (d/L ratios of 1.59–1.83) even with high "dilutions" of the side groups (i.e., with m up to 20). The mesophases were observed in the temperature range from 60 to 97 °C up to 108–152 °C, and the polymers have surface energies lower than PTFE.

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