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Melting and Crystalline Transitions in Normal Perfluoroalkanes and Poly(tetrafluoroethylene)†

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ABSTRACT: Normal perfluoroalkanes containing 6–24 carbon atoms were studied by differential scanning calorimetry. The data indicated that a perfectly crystalline, chain-extended, monodisperse high polymer would have a melting point of 347 °C and a heat of fusion of 24.8 cal/g (104 J/g). Most of the compounds exhibited one or more crystal–crystal transitions between −124 and −70 °C having much smaller latent heats than the room temperature transitions in poly(tetrafluoroethylene). Several approaches point to an equilibrium melting point of 340 ± 1 °C for virgin poly(tetrafluoroethylene).

Studies on normal alkanes have been useful for estimating the properties of perfectly crystalline polyethylene. This subject has recently been reviewed by Mandelkern and Stack.[1] It is of interest to see what a similar approach would do for the analogous perfluorocarbons.

Seven compounds were used in this study. The following materials were purchased from SCM Chemicals: C_6F_{14}, C_7F_{16}, C_8F_{18}, $C_{12}F_{26}$, $C_{16}F_{34}$, and $C_{20}F_{42}$. The remaining compound, $C_{24}F_{50}$, was synthesized by Dr. Walter Mahler of this laboratory. The first three compounds of the series were liquids at room temperature, and the others were crystalline solids. The latter were recrystallized as follows: $C_{12}F_{26}$ from a 60/40 mixture of ethanol and Freon 113, $C_{16}F_{34}$ from Freon 113, $C_{20}F_{42}$ from C_7F_{16}, and $C_{24}F_{50}$ from perfluorodecalin.

The unit cell parameters of the crystals melting above room temperature were determined by X-ray diffraction. Except for spacings corresponding to the lengths of the molecules, diffractometer scans were similar to those for poly(tetrafluoroethylene) (PTFE) above the 30 °C transition where there is extensive torsional motion. The parameters of the hexagonal unit cells are given in Table I. The *a* parameters are similar to that of PTFE at temperatures between 30 and 100 °C.[2] With allowance for the fact that the *c* parameter corresponds to the length of two molecules for $C_{12}F_{26}$ and one for the others, that parameter increases by 1.33 Å for each additional CF_2 group. In PTFE, the length of the unit cell per CF_2 group is 1.30 Å. Even at temperatures just below the melting point, it is increased by less than 1%.[2] Thus, the molecules of the perfluoroalkanes appear to be slightly more extended than the high polymer. Data from Schwickert[3] for the unit cell of $C_{20}F_{42}$ are similar to ours except that his cell corresponds to the length of three molecules.

The thermal properties of the perfluoroalkanes were measured with a DuPont differential scanning calorimeter (DSC) using sealed cups to avoid the loss of material through evaporation and a heating rate of 9 °C/min. The dependences of the melting point, T_m, and the crystal–crystal transition temperatures, T_{cc}, on chain length are shown in Figure 1.

Melting Parameters

The melting points and the heats and entropies of fusion are given in Table II in comparison with those of Schwickert.[3] The data were analyzed according to the treatment of Flory and Vrij.[4] They concluded that a term, $R \ln n$, should be included in the entropy of fusion of long-chain molecules where the chain ends are in an ordered array within the crystal. This term takes account of the mixing of the chain ends with the rest of the material that occurs on melting. In an analysis of several treatments of the melting of long-chain molecules, Mandelkern and Stack[1] concluded that the approach of Flory and Vrij is the best.

Table I
Unit Cell Parameters of Normal Perfluoroalkanes, C_nF_{2n+2}

n	*a*, Å	*c*,[a] Å
12	5.715	35.729 (= 2 × 17.864)
16	5.727	23.089
20	5.700 (5.73 ± 0.05)	28.415 (84. 76 ± 0.05 = 3 × 28.253)
24	5.677	33.821

[a] Values in parentheses from Schwickert.[3]

Careful examination of the DSC scans showed that the change in heat capacity at the melting point is extremely small if not zero for the perfluoroalkanes. Therefore, the terms in ΔC_p in the equations of Flory and Vrij[4] were not included in our calculations. Our data were analyzed with the following expressions taken from the work of Wunderlich and Czornyj:[5]

$$\Delta H_f = \Delta h_e + n\Delta h_f$$

$$\Delta S_f = \Delta s_e + n\Delta s_f + R \ln n$$

$$T_m{}^\circ = \Delta h_f/\Delta s_f$$

The contributions to the heat and entropy of fusion due to the chains ends are Δh_e and Δs_e. Those due to the CF_2 groups are Δh_f and Δs_f. The melting point for an extended-chain crystal of a high polymer is $T_m{}^\circ$. The values computed for these quantities are given in Table III. Plots of ΔH_f, ΔS_f, and $(\Delta S_f - R \ln n)$ vs. *n* are shown in Figures 2 and 3.

The data for C_7F_{16} and C_8F_{18} are clearly out of line with the other points, and they were not included in the least-squares calculations. The only compound having an odd number of carbon atoms was C_7F_{16}. The physical properties of odd and even members of a series frequently follow different patterns. Preliminary X-ray data taken at −79 °C suggest that the crystal structure of C_8F_{18} is not comparable with that of the higher perfluoroalkanes. Since the lines were heavily influenced by the data for C_6F_{14}, alternative calculations were done with and without this compound. The calculated heat of fusion for a high polymer, $\Delta H_f{}^\circ$, is changed very little, but the projected melting point, $T_m{}^\circ$, is reduced by 32 °C (about 5% on the absolute scale) by the inclusion of C_6F_{14}. The value of $\Delta H_f{}^\circ$, 24.8 cal/g (104 J/g), agrees very well with that of 24.4 cal/g (102 J/g) found for virgin PTFE using the Clapeyron equation.[2] The melting point of 347 °C shown in Table III for *n* = 12–24 is only 1 °C higher than that found for virgin PTFE in the earlier study.[2] As discussed above, this may be partially fortuitous because of the limited range of *n* values available. Studies on hydrocarbons[1,4,5] show that a series extending to greater chain

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Table II
Melting Parameters of Normal Perfluoroalkanes

n	T_m,[a] °C	ΔH_f[a] cal/g	ΔH_f[a] J/g	ΔH_f[a] kcal/mol	ΔS_f cal/(deg·g)	ΔS_f cal/(deg·mol)	$(\Delta S_f - R \ln n)$, cal/(deg·mol)
6	−90.7	6.4	27	2.16	0.0350	11.8	8.2
7	−93.3	2.7	11	1.06	0.0152	5.9	2.0
8	−19.0	5.2	22	2.29	0.0206	9.0	4.9
12	75.3 (75)	14.3	60	9.12	0.0411	26.2	21.3
16	129.0 (125)	17.5	73	14.6	0.0435	36.4	30.9
20	164.7 (170)	18.5	77	19.2 (10.7)	0.0423	43.9	37.9
24	192.0	19.5	82	24.1	0.0419	51.9	45.6
PTFE							
virgin	346.3	24.4	102		0.0394		
melted	328.5	22.2	93		0.0368		

[a] Values in parenthesis from Schwickert.[3]

Table III
Contributions to the Heat and Entropy of Fusion

parameter	range of n: 6–24	range of n: 12–24
Δh_e, kcal/mol (kJ/mol)	−5.280 (−22.09)	−5.538 (−23.17)
Δh_f, kcal/mol (kJ/mol)	1.2254 (5.127)	1.2385 (5.182)
r^2	0.9994	0.9990
$\Delta H_f°$, cal/g (J/g)	24.5 (102.5)	24.8 (104)
Δs_e, cal/(deg·mol) (J/(deg·mol))	−3.725 (−15.60)	−2.030 (−8.49)
Δs_f, cal/(deg·mol) (J/(deg·mol))	2.0838 (8.719)	1.9975 (8.358)
r^2	0.997	0.995
$T_m°$, K	588	620
$T_m°$, °C	315	347

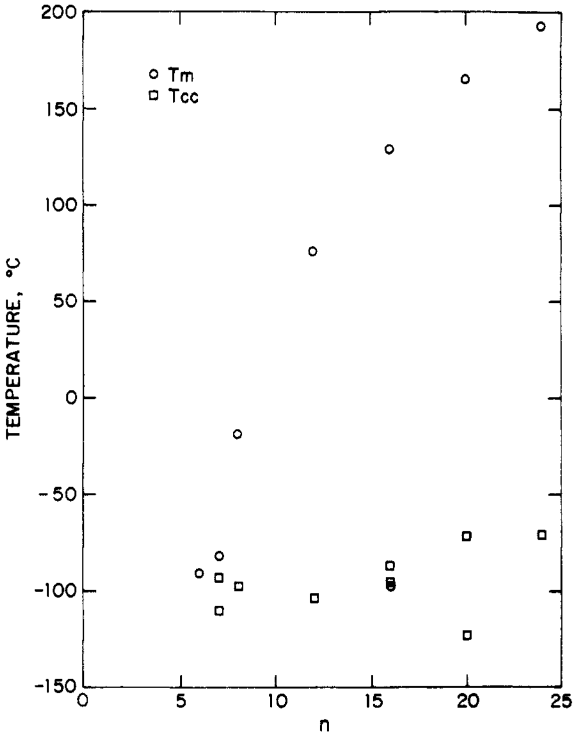

Figure 1. Dependences of the melting point and transition temperatures on chain length.

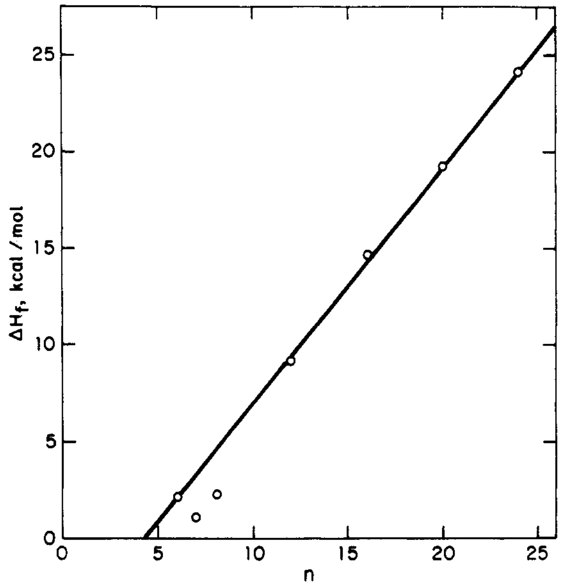

Figure 2. Heat of fusion vs. chain length.

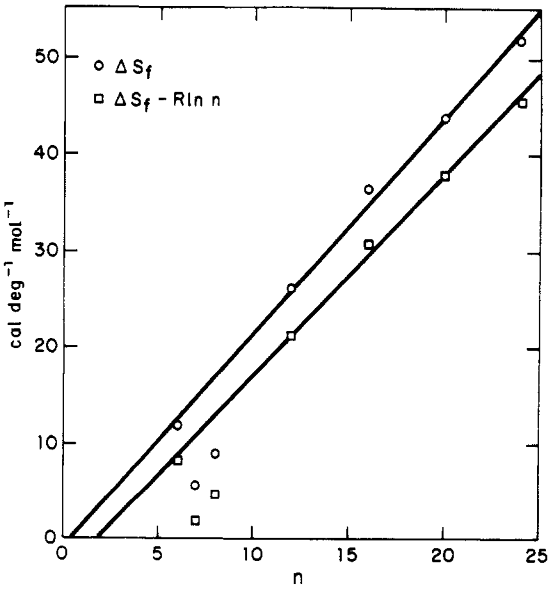

Figure 3. Entropy of fusion vs. chain length.

lengths is desirable if the uncertainty in $T_m°$ is to be minimized.

The importance of including the $R \ln n$ term of Flory and Vrij is clearly demonstrated. Failure to include that term lowered $T_m°$ by 34–40 °C depending on whether the data for C_6F_{14} were included.

It is clear that the melting transition for normal perfluoroalkanes containing 12–24 carbon atoms is closely analogous to that for virgin PTFE. This is supported by the studies of Schwickert on $C_{20}F_{42}$ using X-ray diffraction and vibrational spectroscopy. He concluded that the phase that exists just below the melting point is similar to that which exists in PTFE between the transition at 30 °C and the melting point. However, the lower temperature phases were found not to be comparable for the two materials.

Crystal-Crystal Transitions

PTFE has two crystal-disordering transitions, nominally at 19 and 30 °C. About 90% of the latent heat is asso-

Table IV
Crystal-Crystal Transitions[a]

		ΔH			ΔS	
n	*T*, °C	cal/g	J/g	kcal/mol	cal/(deg·g)	cal/(deg·mol)
7	-110.0	0.37	1.55	0.14	0.0023	0.9
	-93.3	1.62	6.78	0.63	0.0090	3.5
	-81.1	0.73	3.05	0.28	0.0038	1.5
		tot 2.72	11.38	1.05	0.0151	5.9
8	-97.6	1.72	7.20	0.75	0.0098	4.3
12	-103.0	2.58	10.79	1.65	0.0152	9.7
16	-96.7	0.32	1.34	0.27	0.0018	1.5
	-95.5	0.86	3.60	0.72	0.0048	4.0
	-86.5	0.54	2.26	0.45	0.0029	2.4
		tot 1.72	7.20	1.44	0.0095	7.9
20	-123.7 (-132)	0.16	0.67	0.16 (0.18)	0.0010	1.0
	-70.3 (-83)	2.59	10.84	2.69 (0.91)	0.0128	13.3
		tot 2.75	11.51	2.85	0.0138	14.3
24	-70.5	0.75	3.14	0.93	0.0037	4.6
PTFE						
virgin	19	3.10	12.97		0.0114	
melted		4.26	17.82		0.0146	

[a] Values in parentheses from Schwickert.[3]

ciated with the lower transition. All of the normal perfluoroalkanes examined except C_6F_{14}, which melts at -90.7 °C, exhibit one or more first-order transitions below the melting point. As shown in Figure 1, these transitions all occur between -124 and -70 °C. The number and temperatures of the transitions show no particular trend with chain length. There is no tendency to approach the properties of PTFE, at least up to $C_{24}F_{50}$.

The thermodynamic properties of the crystal-crystal transitions are listed in Table IV. Where more than one transition was observed for a compound, the total increases in enthalpy and entropy are given as well as the values for the individual transitions. The values of PTFE are for the combined 19 and 30 °C transitions. The total heats of transition per gram for the normal perfluoroalkanes are lower than the corresponding quantities for either virgin or previously melted PTFE. However, the total entropies in several cases are fairly close to the values for PTFE. It appears that the transitions in the alkanes are different in kind from those in PTFE. One possibility is that the alkane molecules rotate as a whole rather than by segments, as PTFE is believed to do.

Equilibrium Melting Point of Virgin Poly(tetrafluoroethylene)

The melting point of 347 °C obtained by extrapolating data for normal perfluoroalkanes to the high polymer would apply strictly to an extended-chain crystal of a monodisperse polymer in which the chain ends are confined to defined planes. This model may not apply to virgin PTFE. In addition, the significance of the calculation was limited by the long extrapolation from $C_{24}F_{50}$ to the high polymer. In virgin PTFE, the degree of crystallinity is large, and the crystals are believed to be large in the chain direction, a form that cannot be obtained from the melt or solution. Approaches based on the dependence of the melting point of the crystal thickness or the temperature of crystallization are not applicable. For these reasons, a series of experiments was done directly on virgin PTFE.

A sample of virgin PTFE fine powder made by coagulating an aqueous dispersion was heated to a designated temperature, held there for 15 min, quenched to room temperature, and heated to 400 °C at 20 °C/min to determine the heat of fusion. For holding temperatures below the melting interval, the heat of fusion was 77.2 ± 1.3 J/g. For holding temperatures above the melting point, the heat of fusion was 33.0 ± 1.0 J/g. A series of experiments was repeated with initial heating rates of 2 and 20 °C/min. At the faster rate, the temperature overshot by about 0.7 °C and fell back for the 15-min holding period. This overshoot did not occur when the slower heating rate was used in the initial cycle. As shown in Figure 4, the peak temperature in the fast-heating series gave the same behavior as the holding temperature in the slow-heating series even though the time at the peak temperature was only a few seconds instead of 15 min.

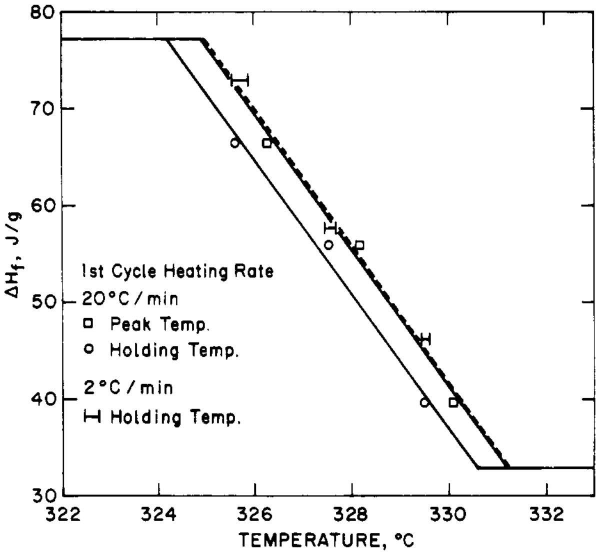

Figure 4. Heat of fusion vs. annealing temperature for virgin PTFE fine powder.

Within a narrow range of temperature, the heat of fusion had intermediate values, and two melting peaks at 325 and 338 °C occurred in the second heating cycle at 20 °C/min. This meant that only part of the material had been melted in the first cycle. The data in the figure show that the melting interval began at 325.0 °C and ended at 331.3 °C.

A similar series of experiments was performed on a high molecular weight granular resin with a heating rate of 2

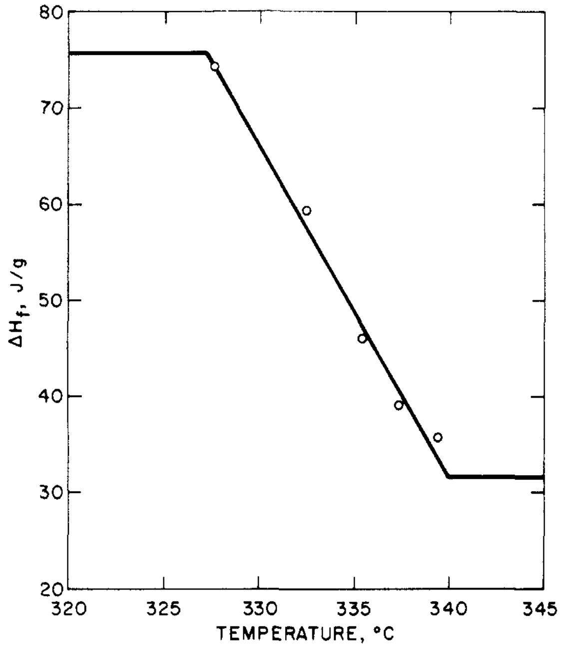

Figure 5. Heat of fusion vs. annealing temperature for virgin granular PTFE.

°C/min in the first cycle. The limiting heats of fusion for low and high holding temperatures were 75.7 ± 4.2 and 31.65 ± 3.4 J/g, and the limiting melting peak temperatures in the second cycles at 20 °C/min were 325 and 344 °C. Intermediate heats of fusion and double melting peaks were found for holding temperatures near 335 °C, as shown in Figure 5. The data indicate that for this polymer, the melting interval begins at 328.6 °C and ends at 339.1 °C.

It is well-known that crystals of PTFE tend to superheat.[6] In a study of the effect of the heating rate on melting behavior,[7] it was found that the DSC melting peak extrapolated to 332 °C for both a virgin fine powder and virgin granular PTFE of relatively low molecular weight at a heating rate of zero. For a higher molecular weight virgin granular polymer, the zero-rate melting peak occurred at 335 °C. In virgin granular PTFE, but not fine powder, the temperature of the zero-rate melting peak correlates with the measured heat of fusion and extrapolates to 341 °C at a value corresponding to 100% crystallinity.[7]

A somewhat different approach to determining the equilibrium melting point was described by Lau, Suzuki, and Wunderlich.[8] They held the polymer at a designated temperature for 12 h, cooled it to 322 °C, and heated it in a DSC at 10 °C/min to determine whether any crystallinity remained. (It was known that 322 °C was above the crystallization temperature for previously melted PTFE). They reported that there was no crystallinity for holding temperatures at or above 331.5 °C. We had been concerned that the 12-h treatments used by Lau and coworkers might have had a deleterious effect on the polymer. The experiments reported here show that much shorter annealing periods are sufficient since times from a few seconds to 15 min gave the same results.

Table V
Determinations of the Equilibrium Melting Point of Virgin Poly(tetrafluoroethylene)

ref	method	temp, °C
this work	melting parameters of oligomers	347
2	end of melting interval extrapolated from high-pressure data	346
7	extrapolation to zero heating rate	
	fine powder	
	DSC peak	332
	DSC end	340.5
	low mol wt granular	
	DSC peak	332
	DSC end	341
	high mol wt granular	
	DSC peak	335
	DSC end	344
7	extrapolation to 100% crystallinity	341
8	annealing	331.5
this work	annealing, end of melting interval	
	fine powder	331.3
	granular	339.1

Various determinations of the equilibrium melting point of virgin PTFE are listed in Table V. Values of 331–332 °C are found for the end of the melting interval of fine powder in the present work, the report of Lau and coworkers,[8] and the temperature of the DSC melting peak extrapolated to a zero heating rate.[7] Nevertheless, we prefer a value of 340 ± 1 °C. Values in this range were found for the end of the melting interval of granular polymer in the present work, the end of the melting interval in DSC experiments extrapolated to a zero heating rate,[7] and in experiments extrapolated to 100% crystallinity.[7]

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Registry No. C_6F_{14}, 355-42-0; C_7F_{16}, 335-57-9; C_8F_{18}, 307-34-6; $C_{12}F_{26}$, 307-59-5; $C_{16}F_{34}$, 355-49-7; $C_{20}F_{42}$, 37589-57-4; $C_{24}F_{50}$, 1766-41-2; poly(tetrafluoroethylene), 9002-84-0.

References and Notes

(1) Mandelkern, L.; Stack, G. M. *Macromolecules* **1984**, *17*, 871.
(2) Starkweather, H. W.; Zoller, P.; Jones, G. A.; Vega, A. J. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 751.
(3) Schwickert, H. Dissertation, Johannes Gutenberg University, Mainz, West Germany, 1984.
(4) Flory, P. J.; Vrij, A. *J. Am. Chem. Soc.* **1963**, *85*, 3548.
(5) Wunderlich, B.; Czornyj, G. *Macromolecules* **1977**, *10*, 906.
(6) Hellmuth, E.; Wunderlich, B.; Rankin, J. M. *Appl. Polym. Symp.* **1966**, *2*, 101.
(7) Starkweather, H. W. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1177.
(8) Lau, S. F.; Suzuki, H.; Wunderlich, B. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 379.