Thermodynamic Properties of Perfluorinated Linear Alkanes and Poly(tetrafluoroethylenes) Measured by PVT and Thermal Analysis[†]

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ABSTRACT: Pressure–volume–temperature data have been obtained for an extensive series of poly(tetrafluoroethylenes) (PTFEs) and PTFE oligomers. The variation of density with MW of the PTFEs is governed by chain end effects, and the results are comparable to the hydrogenated linear alkane series. Dilatometry data of the melting transition in PTFE and oligomers are compared with DSC data on the same samples showing that the premelting region can be characterized in a consistent manner by the two techniques. For three "high" MW PTFE samples, crystallinities were determined by ambient densities of the solids, and also by DSC heats of fusion. From the Clapeyron equation and the measured pressure dependence of the melting points and changes in volume upon melting, the heats of fusion of the fully crystalline oligomers and polymers were estimated.

Introduction

Fluoropolymers such as poly(tetrafluoroethylene) (PTFE) are widely used because of their excellent chemical and temperature resistance. The high melting point (T_m) is partly a result of the reduced entropy gain at the melting point.[1] The unique chemical resistance is due to the very low solubility, especially under ambient conditions.[2-4] Even though the mass density of PTFE is significantly higher (by about a factor of 2) than that of polyethylene (PE), the number density of repeat units (mol repeat units/cm^3) is lower because of the large volume of the F atom compared to H. This reduced number density of repeat units per unit volume or "expanded" state of PTFE compared to PE is what leads to the lower van der Waals forces and the unique low surface energy properties of fluoropolymers.[5] The low molar volume of the PTFE repeat units is also an indication of the low cohesive forces in the solid which result in its unique low friction properties.[1] There are also many similarities between PTFE and PE including the MW dependence of a variety of properties including surface tension,[6,7] melting point,[8] and density.

Pressure–volume–temperature properties have been reported previously[9] for ultrahigh MW PTFE samples of two different crystallinities. Here we report PVT properties for perfluorinated oligomeric to moderate MW PTFE polymers. One ultrahigh MW PTFE sample of low crystallinity is also included to compare with previous literature.[9] From PVT liquid data, bulk liquid properties such as density, compressibility, expansivity, and cohesive energy can be obtained. These thermodynamic properties are the basis for a variety of theoretical predictions including surface tension[6] and phase property calculations of mixtures.[4,10,11]

Experimental Section

Materials. The molecular weights and melting points of the samples studied are listed in Table 1. Perfluorohexane (C_6F_{14}, abbreviated C6) and perfluorododecane ($C_{12}F_{26}$) were gifts of Walter Mahler of DuPont and were essentially pure compounds. PTFE samples with weight average molecular weights of M_w = 1600 g/mol (C31), M_w = 70 × 10^3 g/mol (C1400), and M_w = 27 × 10^4 g/mol (C5400) were gifts from William Tuminnelo of DuPont. The values of M_w for the two higher MW samples were estimated by dynamic rheometry. C31 was fractionated by vacuum distilation and is a moderately polydisperse sample with a M_n estimated from the melting point. Perfluorononane (C_9F_{20}, lot 910840) and perfluoroeicosane ($C_{20}F_{42}$, lot 923053) were obtained from PCR Inc., Gainesville, FL, and were also pure compounds. A commercial grade PTFE sample with very high MW (M_w estimated to be between 10 and 30 × 10^6 g/mol, ca. C400000) was taken from a block of Teflon.

Samples for PVT and DSC measurements were crystallized by cooling from the melt at 1–10 °C/min. Solvent crystallized samples, such as those studied previously,[8] were not studied. The low MW samples obtained after cooling from the melt were very brittle because of high internal stress due to the volume change during crystallization. In most cases, better quality samples in terms of low void fraction were obtained by pressurizing a 5 g sample into a solid plug at 25 °C using a mold and a metal rod with a cross sectional area of ~1 cm^2. Plugs of C12, C20, and C31 for PVT measurements were prepared in this manner. C6 and C9 were liquids at room temperature.

Methods. PVT properties were obtained with the methods described previously[12] using an instrument which was obtained from Gnomix Research, Boulder, CO. Densities of PTFE and oligomers at 25 °C were measured using density bottles for liquids and an autopycnometer (Micrometrics) for solids. For accurate results the room temperature sample density must be measured very carefully and solid samples must be prepared free of voids. Room temperature densities are required as input to calculate the absolute values of the specific volume, V_{sp} (= 1/ρ), determined as a function of T and P using the PVT dilatometer.

For the liquid PVT properties in the Appendix, the data were taken in the "isothermal" mode where values of V_{sp} were measured at constant temperature as the pressure was incremented in 10 MPa jumps to a maximum of 200 MPa. For each temperature increment the pressure was then released to 10 MPa (1 MPa = 9.87 atm) and the cycle started over again. 10 MPa was the lowest pressure at which actual data were taken. All values of V_{sp} reported here at 0.1 MPa were values extrapolated using the Tait equation. Even though only liquid data are presented in the Appendix, full data sets from room temperature to $T \gg T_m$ were obtained in this isothermal mode (see below). For other studies of melting, isobaric heatings and coolings were performed at different rates between 0.5 and 5 °C/min.

Thermal analysis was performed with a DuPont 9900 DSC station.

[†] Dedicated to Howard W. Starkweather on the occasion of his retirement after 42 years of service at DuPont.

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Table 1. MW, Crystallinity, and Melting Transitions in PTFE and Oligomers

	M_n[a]	M_w[a]	T_m (°C)	$\Delta H_{(DSC)}$ (J/g)	$W_{c(DSC)}$	$W_{c(Dens.)}$[b]	ΔV_m (cm^3/g)	dT_m/dP (°C/MPa)	$\Delta H_{f,o}$ (J/g)
C6	338	338	−90[c]						
C9	488	488							
C12	638	638	78	43	0.72[d]		0.082[e]	0.481	60
C20	1038	1038	167	57	0.74[d]		0.106[e]	0.68	81
C31	1600	–	219	53			0.112[e]	0.65	83
C1400	–	70×10^3	332	78	0.84	0.94	0.176[e]	0.883	119
C5400	–	27×10^4	331	69	0.74	0.77	0.152[e]	1.0	92
C400000	–	20×10^6	334	40	0.43	0.44	0.120[f]	1.17	–
Literature (ultrahigh MW PTFE)[g]			329	37	0.40	0.40	0.149[h]	0.97	93

[a] M_n and M_w are the number and weight average molecular weights, respectively. [b] Crystallinity calculated from ambient density data. [c] Taken from ref 8. [d] Calculated from $\Delta H_{f,o}$ values from ref 8. [e] $\Delta V_m = V_1 - V_c$ where the crystal specific volume (V_c) is taken directly from the *PVT* data for the solid which is assumed to be 100% crystalline (see the text). [f] This sample is clearly not fully crystalline so the *PVT* solid data are not a good estimate for V_c. This is why this value is smaller than $\Delta V_m = 0.149$ from ref 9. [g] Data for this once melted PTFE sample were taken from ref 9. [h] These results were taken from ref 9, where in the melting point was calculated from X-ray parameters. All other values of V_c which were used to calculate ΔV_m in this table were determined from our *PVT* parameters assuming the solids were 100% crystalline.

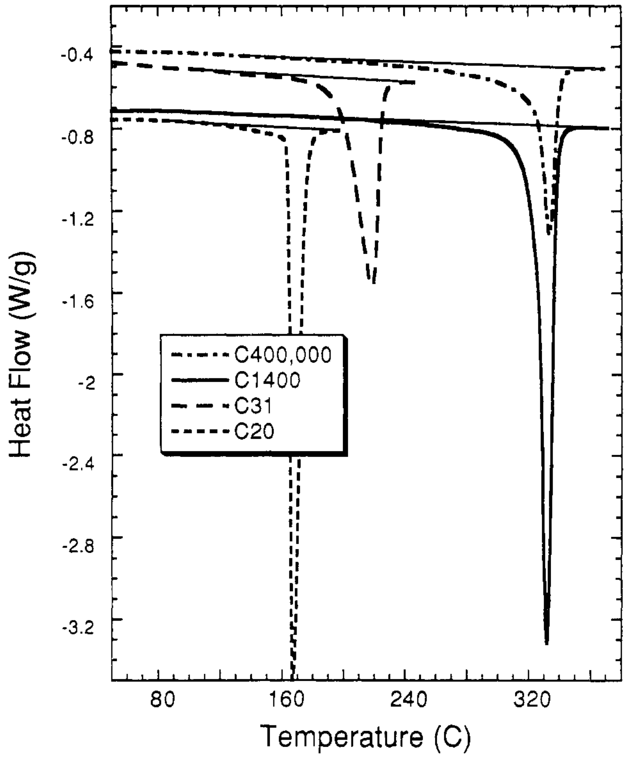

Figure 1. DSC data at a heating rate of 20 °C/min for C20, C31, C1400, and C400000.

Results

DSC. DSC data are given in Figure 1 for four different MWs. Systematic DSC data for high MW PTFE of varying crystallinities have also been reported earlier.[13] Peak melting points for PTFE and oligomers are listed in Table 1. A significant premelting and broadening of the endotherm is seen for C31 because of its polydispersity, as compared to the very sharp endotherm observed for the more monodisperse C20. The MW of C31 is in the range where T_m is extremely dependent on MW.[8] For higher MWs (number of carbons greater than ca. 100), T_m has already reached the high MW limit, and kinetic effects rather than polydispersity in MW contribute to broadening. The substantial premelting fraction seen as a shoulder on the low-temperature side of the main transition for C400000 occurs because the very high MW gives rise to low mobility of chains in the melt leading to a high population of defective crystals. It is these defective crystals that contribute to the observed premelting (Figure 1). The onsets of premelting, as determined from the departure from the DSC baseline (Figure 1), are summarized in Table 2.

Table 2. Comparison of the Onset of Melting (Premelting) Determined by DSC and PVT

	$T_{m,onset}$ (°C)			$T_{m,onset}$ (°C)	
	DSC	PVT		DSC	PVT
C12	74	70	C1400	230	270
C20	162	157	C5400	250	250
C31	110	100	C400000	130	140

The heats of fusion (ΔH_f) for each sample, determined from integration of the DSC endotherms, show a maximum with increasing MW. The lowering in crystallinities (or densities) for melt-crystallized samples with MWs above C8000 has been well-documented[1] and are again due to kinetic constraints restricting crystallization. For high MW PTFEs (i.e., C1400, C5400, and C400000), the crystalline fraction [$W_{c(DSC)}$] can be calculated from ΔH_f using the literature heat of fusion for 100% crystalline PTFE ($\Delta H_{f,o}$) which was reported to be 93 J/g.[9] The results (Table 1) indicate that C1400 and C5400 are close to 100% crystalline while C400000 is significantly lower, as expected.[1] In the calculation of ΔH_f, the full endotherm was integrated including the premelting regions.

Starkweather[8] has given values of $\Delta H_{f,o}$ = 60 J/g determined by DSC for solution-crystallized C12 which is essentially 100% crystalline. Using the measured value of ΔH_f = 43 J/g (Table 1) for our melt-crystallized C12, the percent crystallinity is calculated to be on the order of $W_{c(DSC)}$ = 0.72. Using analogous data from the same paper, a value of $W_{c(DSC)}$ = 0.74 is determined for our melt-crystallized C20 sample.

Solid State Density. The ambient pressure and temperature densities of the high MW PTFE samples can be used to estimate the volume fraction crystallinity [$W_{c(Dens.)}$] in the melt-crystallized samples. For this calculation, densities of 2.060 and 2.302 g/cm^3 are assigned the purely amorphous and crystalline materials, respectively, at 20 °C.[1,13] This amorphous density of 2.060 g/cm^3 taken from the work of Starkweather[13] is different than the one used previously.[9] The values of $W_{c(Dens.)}$ are calculated by extrapolation of V_{sp} (= $1/\rho$) between these amorphous and crystalline values. It is seen from Table 1 that the calculated values of $W_{c(Dens.)}$ are comparble to those determined by $W_{c(DSC)}$.

For some PTFE oligomers, the amorphous phase densities at room temperature are not known so values of $W_{c(Dens.)}$ were not calculated (Table 1).

PVT. Representative data taken in the "isothermal" mode are shown for C12, C20, C31, and C1400 in Figures

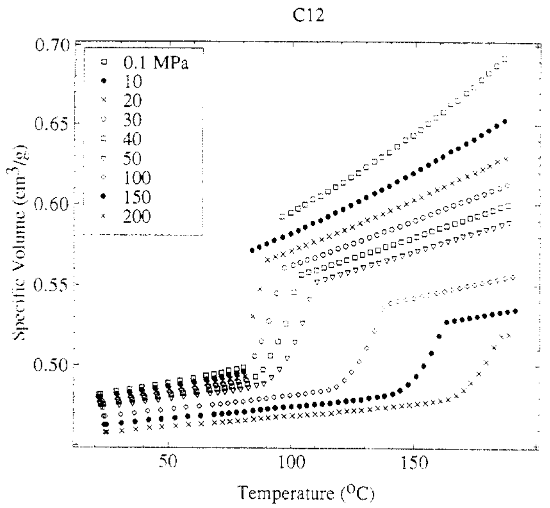

Figure 2. Specific volume of originally melt-crystallized C12 vs temperature for the different pressures indicated. The data were taken in the "isothermal" mode and the 0.1 MPa data are extrapolated. (see Experimental Section).

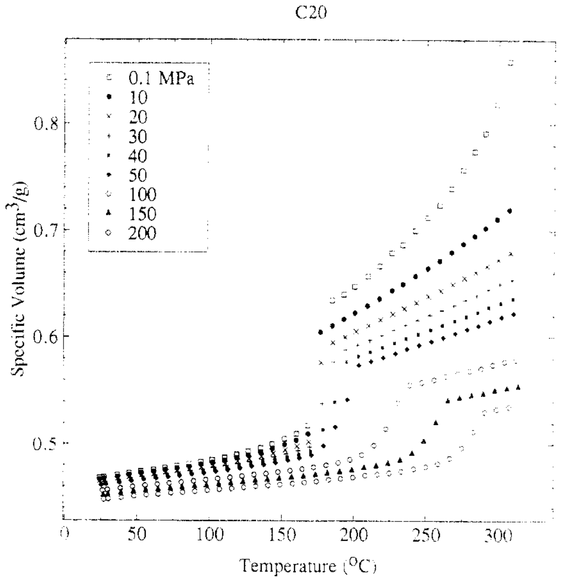

Figure 3. Specific volume of originally melt-crystallized C20 vs temperature for the different pressures indicated. The data were taken in the "isothermal" mode and the 0.1 MPa data are extrapolated. (see Experimental Section).

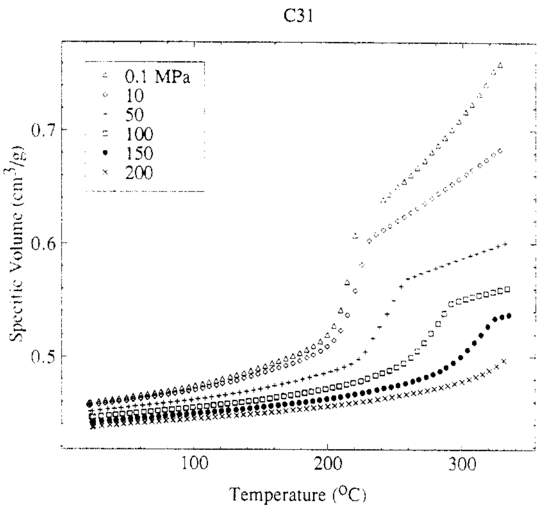

Figure 4. Specific volume of originally melt-crystallized C31 vs temperature for the different pressures indicated. The data were taken in the "isothermal" mode and the 0.1 MPa data are extrapolated. (see Experimental Section).

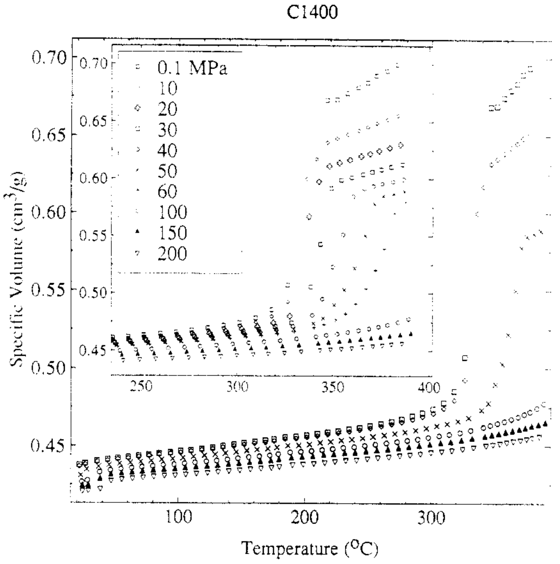

Figure 5. Specific volume of originally melt-crystallized C1400 vs temperature for the different pressures indicated. The inset gives an expanded view of the melting region and its variation with pressure. The data were taken in the "isothermal" mode and the 0.1 MPa data are extrapolated. (see Experimental Section).

2–5. To our knowledge, PVT data are not available for most PTFE oligomers. From melt PVT data, bulk liquid properties such as density, compressibility, expansivity, and cohesive energy can be extracted. PVT properties for high MW PTFE melts have been reported previously[9] and are consistent with those reported in the Appendix. The liquid PVT properties for all of our perfluorinated samples can be extracted from the tables of data in the Appendix. It is evident from the raw data (Figures 2–5) that the expansivities [$V_{sp}^{-1}(dV_{sp}/dT)$] of the melts are a strong function of temperature, contrary to what is normally assumed. The same is true for the compressibility. Accurate representation of the properties is possible using these full data sets but is often neglected when using the data for theoretical predictions.

To compare the solid state properties as a function of MW, isobaric scans at 10 MPa (1 MPa = 9.87 atm) are shown in Figure 6 for several of the samples. Significant departures from the low-temperature baselines are seen for C31 and C400000, as is indicated by the lines drawn through the data. Both PVT and DSC data indicate that this premelting region is minimized for C12, C20, C1400, and C5400 whereas it is significant for C31 and C400000. The transitions are broad for C31 because of its polydispersity[8] and for C400000 because of defective crystals formed due to mobility constraints as was discussed above. Slight departures from the baselines of the solid region are seen for C1400 and C5400 just before the main melting. These are also signs of early melting of a small fraction of imperfect crystals. Table 2 shows that the estimates of the onset of premelting are consistent, as determined by both PVT (at 10 MPa) and DSC for all MWs considered.

The volume changes upon melting first increase with increasing MW and then decrease again for the highest MW (C400000 in Figure 6). This is consistent with the DSC determination of the degree of crystallinity. The overall crystallinity in C400000 is much lower because the extremely high MW leads to kinetic constraints which severely limit crystallization from the melt. The crystallinity is known to be low in melt-crystallized ultrahigh MW polyethylene for the same reason.[15]

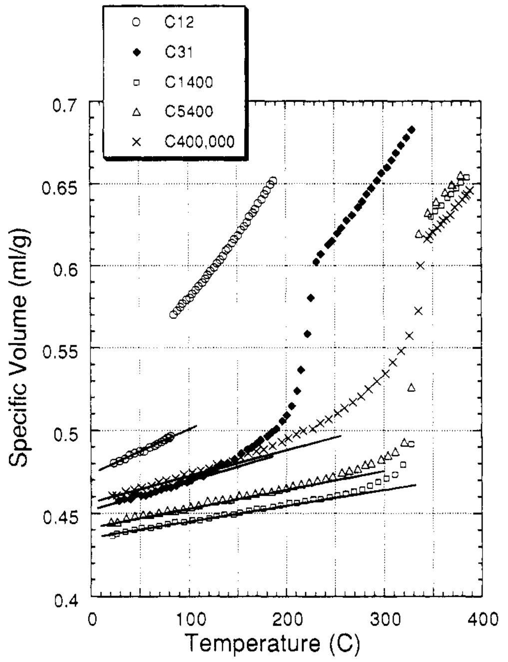

Figure 6. Specific volume (V_{sp}) taken in the "isothermal" mode vs temperature at 10 MPa for selected PTFEs and oligomers showing the solid and liquid regions.

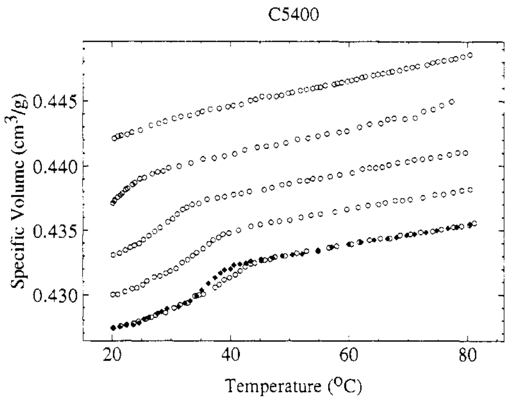

Figure 7. Isobaric heating scans of V_{sp} in C5400 at 40, 80, 120, 160, and 200 MPa from top to bottom, respectively. The solid symbols for 200 MPa are for a isobaric cooling showing the expected hysteresis for a first-order phase transition.

The data taken in the "isothermal" mode (Figures 2–5) also show an interesting broadening of the main melting region as the pressure is increased. This is especially evident for C12 and C20 for which the melting regions are quite sharp at 10 MPa. Substantial hysteresis, seen upon isobaric heatings and coolings, allow us to conclude that the broadening observed is actually a kinetic effect because of finite crystal nucleation rates. Because the "isothermal" data are taken during pressurizing cycles (see Experimental Section), the transitions that are seen at pressures greater than 10 MPa (Figures 2 and 3), are actually due to crystallization during pressurization. Thus, the finite crystallization rate actually causes the broadening.

The well known "room temperature" transitions were routinely observed in PVT studies of C1400 and C5400. Since these are crystalline transitions observed mainly in moderate to high MW PTFE,[14,16] they are most prominent for our high-crystallinity samples. Both the 19 and 30 °C transitions have been studied previously by dilatometry[17,18] and thermal expansion.[18] The 19 °C transition is a first-order phase transition and corresponds to a change in the helical chain conformation in the crystal. It is found by these methods to be many times stronger than the 30 °C transition. A phase diagram has been reported based on literature data above 0 °C.[1,19] Isobaric heating scans of the 19 °C transition are shown in Figure 7. Low-temperature data cannot be easily obtained on our PVT instrument, so we only observed the 19 °C transition at higher pressures. The lowest pressure shown in Figure 7 is 40 MPa, and at this pressure the transition is barely out of range. At higher pressures one observes a strong pressure dependence of the transition. The extrapolated value of the endpoint of the transition at 0.1 MPa is calculated to be 16 °C. We find no evidence of the 30 °C transition at the pressures used in our studies. The variation of the 19 °C transition with pressure is 0.014 ± 0.001 °C/atm or 0.138 °C/MPa, consistent with previous data.[1]

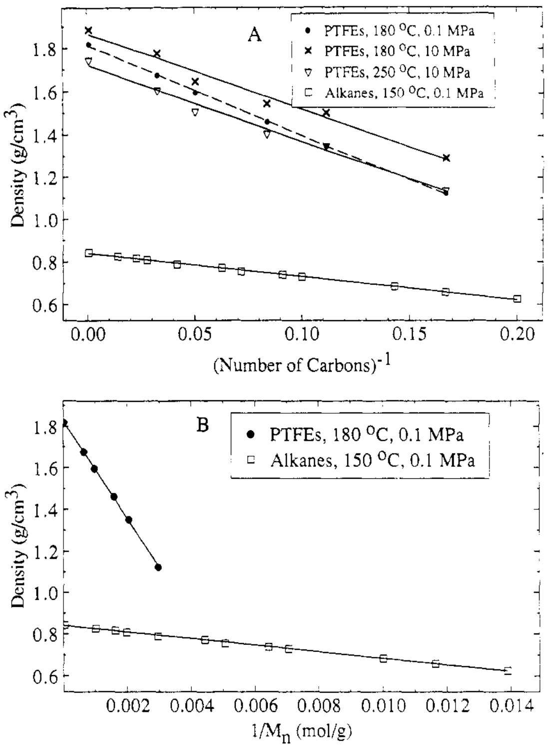

Figure 8. The atmospheric liquid densities for linear perfluorinated alkanes (PTFEs) and linear alkanes (PEs) are plotted vs the reciprocal number of carbons (A) and reciprocal molecular weight (B). (see the text).

Discussion

The atmospheric liquid densities are plotted vs the reciprocal number of carbons and $1/M_n$ in Figure 8. Data for linear alkanes including polyethylene are included.[20] T_m for the perfluorinated alkanes vary so rapidly with MW that it is not possible to obtain overlapping liquid densities at a constant temperature over the entire MW range. Thus, some extrapolations were needed to obtain the data in Figure 8. For example, rather long extrapolations from the 0.1 MPa melt data of C1400 (Figure 5) to temperatures of 180 °C are needed. In order to perform this extrapolation, we assumed that the curvature in V_{sp} vs T was comparable to that for some of the lower MWs. Thus, the data points for C1400 in Figure 8 should be interpreted with some caution. The extrapolation of the melt V_{sp} for C1400 to 250 °C at 10 MPa has less error because the 10 MPa data are more linear and the extrapolation is shorter.

Figure 8A shows that the PTFE and PE series are quite similar. The relative percent variation in density with chain length are comparable (Figure 8A), as was the case with melt surface tensions.[6] The variation with chain length is simply due to the well-known effect[20,21] of the higher molar volume of chain ends compared to chain center units. Changing the molecular weight changes the number density of chain ends and this is why the properties vary with reciprocal M_n. The slopes for both series will vary depending on the choice of temperature because of the MW dependence of the thermal expansion coefficient. Thus, any trends seen in the slopes in Figure 8A between PFFE and PE can be reversed by changing the temperature. The density plots actually become nonlinear at high temperatures for the PE series for reasons related to chain end effects as was discussed previously.[20] Figure 8B shows the density vs $1/M_n$. The differences in slopes are exaggerated because of the higher mass per chain unit of the PTFE series.

One can also use the change in V_{sp} in the melting region to examine the influence of MW on crystallization and melting. Starkweather et al.[9] studied ultrahigh MW PTFE samples of different crystallinity and reported values for dT_m/dP of 0.97 °C/MPa [equivalent to 0.095 °C/(kg/cm^2)]. The pressure dependence of the values of T_m, where T_m is defined as the end of melting,[9] were used to define dT_m/dP in our studies. The values that we have obtained for the various MWs are compared in Table 1. The values for high MW PTFE agree with those reported earlier.[9] The values of dT_m/dP are smaller for the lower MW samples (Table 1).

The Clapeyron equation is used at 0.1 MPa for the heat of fusion of a 100% crystalline sample ($\Delta H_{f,o}$ in J/g and T_m in K).

$$\Delta H_{f,o} = T_m \Delta V_m \, (dT_m/dP)^{-1} \tag{1}$$

$\Delta V_m = V_l - V_c$, and V_l and V_c are the specific volumes (V_{sp}) of the liquid and the 100% crystalline solid, respectively. For the two moderate MW PTFE samples (C1400 and C5400), which we assume to a first approximation to be 100% crystalline, V_c is obtained from the solid state PVT data, correcting for premelting. V_l is obtained from the PVT liquid data (Appendix) and the resulting ΔV_m values are given in Table 1. Previously, the X-ray unit cells determined at the appropriate temperature were used to determine the 100% crystalline density, V_c^{-1}. Table 1 lists this literature value of ΔV_m and it is found that it is roughly consistent with those for C1400 and C5400. Table 1 indicates that the values of $\Delta H_{f,o}$ calculated with eq 1 for C1400 and C5400 are also roughly consistent with the literature.

According to eq 1, $\Delta H_{f,o}$ is actually not constant as a function of P since dT_m/dP is essentially constant with P, and ΔV_m varies much more rapidly with P than does T_m (in degrees kelvin). This is because of the difference in the compressibilities of the crystal and the liquid. Corrections would be needed to account for the reduced volume of the liquid compared to the solid in order to apply eq 1 at higher pressures.

For the oligomers, we again assume to a first approximation that the solid is essentially 100% crystalline, so $\Delta V_m = V_l - V_c$ is determined entirely from the PVT data. With this assumption, values for $\Delta H_{f,o}$ are obtained (Table 1) and found to be quite similar to those measured by DSC on solution-crystallized C12 and C20 samples.[8] DSC may give *slightly* lower values for ΔH_f (Table 1) than these values of $\Delta H_{f,o}$, because of pressure recrystallization effects during the collection of PVT data in the isothermal mode.

Table 3

T_{min}	T_{max}	P^* (MPa)	V_{sp}^* (mL g^{-1})	T^* (K)	S^2 (MPa^2)
			C6		
30.0	42.8	421.8	0.42594	3895.7	0.150
45.1	58.3	376.8	0.43221	3990.5	0.144
60.6	73.3	385.0	0.43161	3996.6	0.104
75.3	88.0	375.9	0.43323	4025.2	0.112
89.9	103.8	364.2	0.43530	4053.7	0.114
			C9		
61.3	73.4	399.4	0.42011	4451.6	0.203
73.9	85.8	397.3	0.42081	4482.4	0.136
86.2	98.4	390.7	0.42204	4517.5	0.100
98.6	111.4	374.2	0.42465	4571.8	0.083
111.2	123.9	375.1	0.42498	4592.1	0.058
123.7	136.4	378.8	0.42497	4608.9	0.033
135.8	149.0	360.9	0.42800	4653.1	0.042
148.3	161.3	362.5	0.42821	4666.4	0.033
160.8	173.8	365.2	0.42837	4682.2	0.055
172.9	186.0	338.8	0.43297	4726.5	0.028
185.4	198.4	380.2	0.42767	4716.1	0.075
			C12		
102.0	119.4	362.9	0.43064	5024.5	0.04
119.4	136.8	358.3	0.43192	5053.1	0.03
136.8	154.2	353.0	0.43318	5079.1	0.03
154.2	171.6	357.4	0.43309	5083.3	0.04
171.6	189.0	335.1	0.43698	5145.5	0.04
			C20		
175.0	205.0	369.8	0.43016	5595.6	0.04
205.0	235.0	341.6	0.43572	5697.1	0.04
235.0	265.0	333.7	0.43851	5755.1	0.05
265.0	295.0	329.1	0.44049	5800.1	0.09
295.0	312.0	298.5	0.44722	5870.2	0.08
			C31		
235.0	260.0	354.2	0.42200	6034.4	0.01
260.0	285.0	350.0	0.42560	6118.7	0.07
285.0	311.0	368.1	0.42430	6130.1	0.17
311.0	333.0	351.1	0.42841	6212.7	0.10
			C1400		
346.0	387.0	325.4	0.43353	7203.3	0.06
			C5400		
352.0	384.0	374.8	0.425315	7003.2	0.26
			C400000		
351.0	389.0	411.2	0.415305	7040.6	0.1

Conclusions

Melt densities of a PTFE homologous series were compiled vs reciprocal molecular weight and are shown to exhibit similar behavior when compared with homologous linear alkane series. As is the case with many materials, the variation of density with MW is due to the higher molar volume of chain ends. Comparison of PVT data of the melting transition in PTFE and oligomers with DSC data on the same samples shows that the premelting region can be characterized in a consistent manner by the two techniques. In one oligomeric sample, polydispersity was shown to contribute to a significant premelting region in addition to a broadening of the main melting transition due to the strong dependence of T_m in this range of MWs. PVT data were also obtained for the room temperature crystal transition in high MW PTFE as a function of pressure. For the three "high" MW PTFE samples studied, crystallinities were determined by ambient densities of the solids, and also by DSC heats of fusion. From the Clapeyron equation and the measured pressure dependence of the melting points and changes in volume upon melting, the heats of fusion of the fully crystalline oligomers and polymers were estimated.

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Mahler, William Tuminello, S. Mazur, and William Kampert, for their important contributions.

Appendix

The Flory, Orwoll, and Vrij model[22] was found to provide a good description of the polymer liquid data sets. The form of the equation is shown below:

$$\tilde{P}\tilde{V}/\tilde{T} = \tilde{V}^{1/3}/(\tilde{V}^{1/3} - 1) - 1/(\tilde{T}\tilde{V}) \qquad \text{(A1)}$$

where $\tilde{P}$, $\tilde{T}$, and V are the reduced pressure, temperature, and volume which are defined as follows: $\tilde{P} = P/P^*$, $\tilde{T} = T/T^*$, and $\tilde{V} = V_{sp}/V_{sp}^*$, where V_{sp} is the specific volume, and P^*, T^*, and V_{sp}^* are the reduction parameters which are obtained by fitting eq A1 to blocks of PVT data.

Blocks of PVT data were fitted to eq A1 for 10 MPa < P < 100 MPa and for the ranges of temperatures shown in Table 3. The temperature ranges were selected so that the value of S^2 is of the order of 0.1 and is defined by

$$S^2 = \sum (P_{data} - P_{fit})^2/(N - 3) \qquad \text{(A2)}$$

where P_{data} is the measured pressure at a given temperature and specific volume, P_{fit} is the pressure predicted by eq A1, and N is the number of data points. Values of S^2 of the order of 0.1 are equivalent to errors in the V_{sp} of the order of 1.0×10^{-3} mL g^{-1}. Therefore, using the parameters in Table 3, one can reconstruct the original melt data with an accuracy on the order of the accuracy of the experimental data. The lowest pressure at which actual experimental data were taken was 10 MPa. It has been shown that significant errors can occur when extrapolating data to ambient pressure (0.1 MPa), especially for derivative quantities such as expansivity and compressibility.[23] In some cases where actual experimental 0.1 MPa data were available to compare with, data extrapolated from PVT using the FOV model were shown to be quite accurate.[24]

The raw PVT data files for these and other materials are available from the authors upon request.

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