rather than the portion far removed from that interface, is much less sensitive to the intramolecular short-range interactions. Similar segregation of the short branches is seen in simulations with and without intramolecular energetic terms.

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Observation of a New High-Temperature Transition in Polytetrafluoroethylene

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ABSTRACT: We wish to report that in sintered polytetrafluoroethylene (PTFE), there is an order → disorder transition at 370 ± 10 °C which otherwise has been known to show the highest temperature (melting) transition at 327 °C since its discovery over 50 years ago. The intensity of the 370 °C transition varies from sample to sample, and at present we are not fully aware of the factors responsible for its selective formation except that a high molecular weight and moderate shear stresses in the solid ↔ melt region are required. Limited experimental data available suggest that the loss of helical order occurs at ~327 °C and at ~370 °C the loss of equatorial order takes place; the latter existing in the presence of molecular constraint created from shear stresses on a high molecular weight resin. Differential scanning calorimetry, rheology, hot-stage optical microscopy, variable-temperature X-ray diffraction, and infrared data are presented to demonstrate these findings.

Introduction

The melting, crystallization, and morphology of PTFE and their relationship to molecular weight have been discussed in the papers of Suwa et al.[1,2] At a heating rate of 8 °C/min, their differential scanning calorimetry (DSC) results suggest a melting peak temperature (T_m) between 335 and 341 °C for the virgin PTFE. The sintered PTFE exhibits a T_m at 327 ± 1 °C. Wunderlich[3] claims an equilibrium melting temperature (T_m^0) of 327 °C for PTFE. Thus, although the T_m^0, i.e., melting of perfect crystals, is accepted to be 327 °C, depending upon the sample history and experimental conditions, one can come across a melting temperature as high as about 341 °C for PTFE as a result of superheating.[4] Recently we have commented upon the melting temperatures of PTFE, i.e., 327 vs 341 °C, and proposed a T_m^0 = 334 °C.[5] References 4 and 5 are recommended for a discussion of the superheating in PTFE.

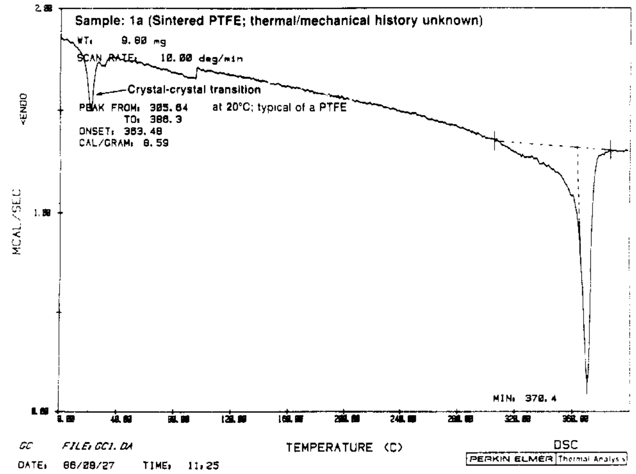

Figure 1. DSC thermogram (10 °C/min) showing the 370 °C transition in a sintered PTFE (sample 1a; thermal/mechanical history unknown).

On August 27, 1986, we became aware of an unusual high-temperature transition (melting) in PTFE at 370 °C (e.g. see Figure 1). As we are getting ready to send this paper, we have come across a reference by Grebowicz et al.[6] which mentions the 370 °C transition. The major differences between Grebowicz et al.[6] and our studies are as follows: (1) they report only a trace peak at

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Table I
Description of PTFE Samples Used in Our Study

sample no.	descriptn		transitn temp, °C
1	a sintered, cylindrical article made from a commercial powder		332 + ?
1a	a portion of sample 1 used in a thermal conductivity apparatus; thermal/mechanical history unknown		? + 370 ? + 370
2	a commercially sold PTFE tape		339 + 379[a]
3	a sintered piece	some grade of a commercial resin	331 + 363[a]
4	sintered films		330 + ?
5			330 + ?
6	virgin powders		344 + ?
7			344 + ?
8	a sintered piece molded at 400 °C		329 + ?
9	powder extruded at 350 °C moderate shear rates		334 + 353 + 380 335 + 350 + 379

[a] A small fraction.

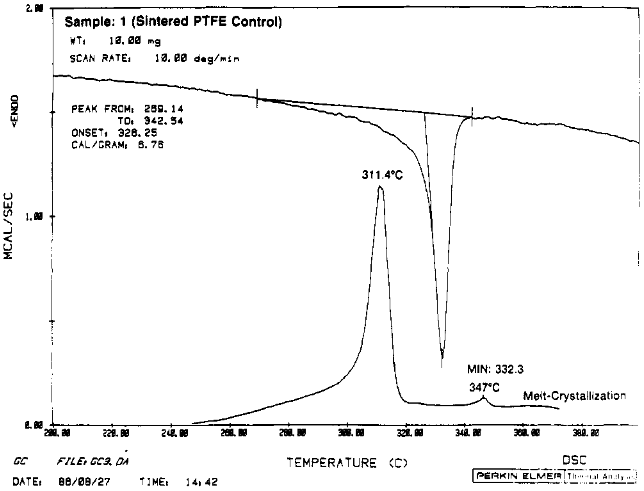


Figure 2. DSC thermogram (10 °C/min) showing the typical 330 °C melting peak in a sintered PTFE (sample 1; control for sample 1a).

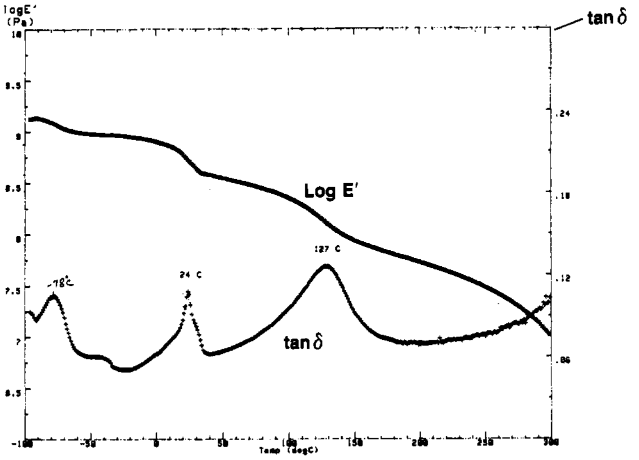


Figure 3. DMA thermogram (3 °C/min, 1 Hz) showing the typical relaxations of PTFE (sample 1a; thermal/mechanical history unknown).

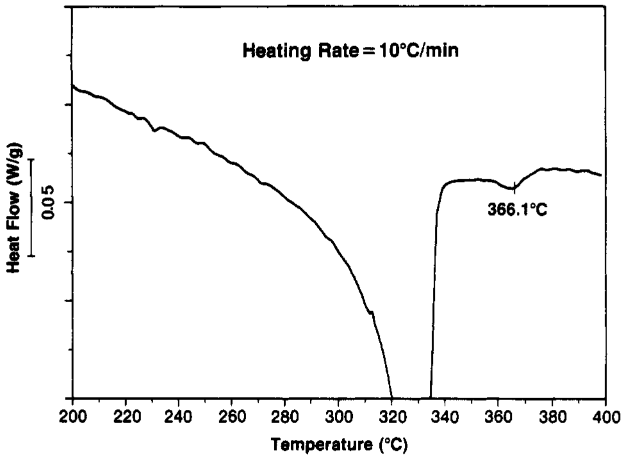


Figure 4. Expanded scale DSC thermogram (10 °C/min) showing a trace T_{od} at ~365 °C in a sintered PTFE (sample 1).

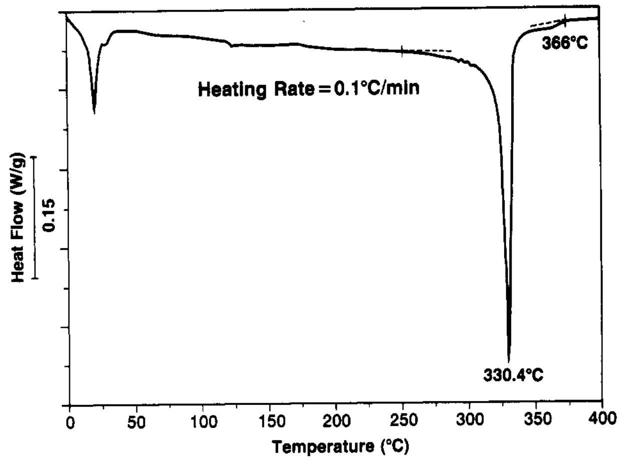


Figure 5. DSC thermogram at 0.1 °C/min heating rate showing a trace T_{od} at ~365 °C in a sintered PTFE (sample 1).

370 °C, whereas we have shown that the 370 °C peak can be either a trace, significant fraction, or the only peak (2) we have identified the processing conditions to introduce the morphology with the major melting peaks at 353 and 380 °C in sintered PTFE samples. In contrast, if the samples of Grebowicz et al.[6] had been sintered at 350 °C like ours, these would have only a trace peak at 380 °C, and (3) only on the basis of DSC, Grebowicz et al.[6] attribute the 370 °C peak to the melting whereas our multianalytical study suggests the 370 °C transition to be due to the disruption of two-dimensional order.

Experimental Section

Materials. All the samples used in this study were of commercial grade (Table I). The samples were characterized in terms of the number-average molecular weight (M_n) using the following relationship based on the data from Suwa et al.:[1]

$$\log \Delta H_c = (-0.1743) \log M_n + 1.89$$

where ΔH_c is the heat of crystallization of sintered PTFE obtained by DSC.

Characterization. Differential scanning calorimetry experiments were carried out by using a Perkin-Elmer DSC-2C or Du Pont 9900 instrument in argon atmosphere and a sample size of 10.0 ± 0.2 mg in crimped Al pans. The program rate for the "heating/cooling (after 380 °C/5 min treatment)/reheating" scans was 10 °C/min unless otherwise specified. The instrument was calibrated by using lead melting standard such

Table II
Effect of Molecular Weight on the High-Temperature Transition ($T_{od} \simeq$ 365 °C/$T_{d_o} \simeq$ 346 °C) in PTFE[a]

sample			melt crystallization (after 380 °C/5 min)		
no.	source	phys form	peak temp, °C	heat evolved, ΔH_c, cal/g	mol weight[c] (M_n) × 10^{-6}
4	? (U.S.A.)	sintered film	$\underline{311}$ + 347	5.8 (±0.3)	2.91 (?)
5			$\underline{311}$ + ?	6.7 (±0.4)	1.27 (?)

[a] Data for samples 1–3 is presented in Figures 1–6. [b] Calculated according to the method of Suwa et al.[1] and recommended for following the relative changes only.

Table III
Effect of Molecular Weight on the High-Temperature Transition ($T_{od} \simeq$ 365 °C/$T_{d_o} \simeq$ 346 °C) in PTFE

sample			melt crystallization (after 380 °C/5 min)			melt crystallization (after 450 °C/5 min)		
no.	source	phys form	peak temp, °C	ΔH_c, cal/g	(M_n) × 10^{-6} [a]	T_{cc}, °C	ΔH_c, cal/g	(M_n) × 10^{-6} [a]
6	? (U.S.A.)	virgin powder	$\underline{312}$ + 346	5.5	3.94 (?)	306	11.7	0.05 (?)
7			$\underline{312}$ + 345	5.9	2.64 (?)		11.1	0.07 (?)

[a] Calculated by the method of Suwa et al.[1] and recommended for following the relative changes only.

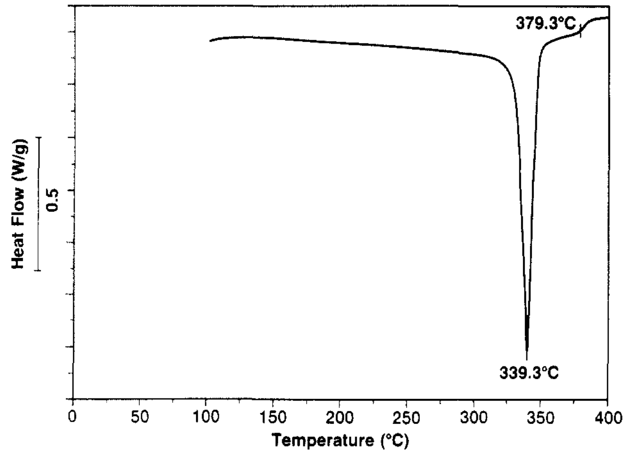


Figure 6. DSC thermograms (10 °C/min) showing a trace T_{od} at ~379 °C in a commercially sold PTFE tape (sample 2).

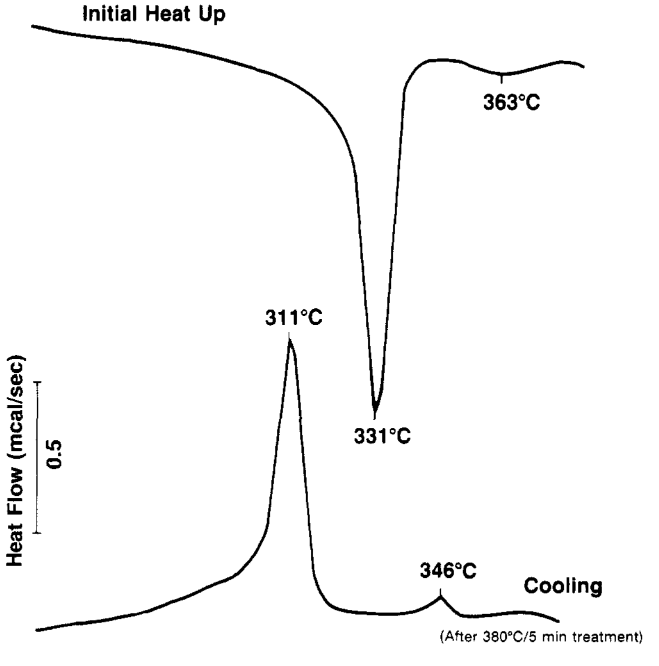


Figure 7. DSC thermograms (10 °C/min) showing the melting and melt-crystallization curves of a sintered piece of PTFE (sample 3).

that its onset of melting was within ±1 °C of the literature value.

Dynamic mechanical analysis was carried out on a Polymer Laboratories DMTA unit using the following conditions: argon atmosphere, bending deformation, 1-Hz frequency, <1% strain, and 3 °C/min heating rate.

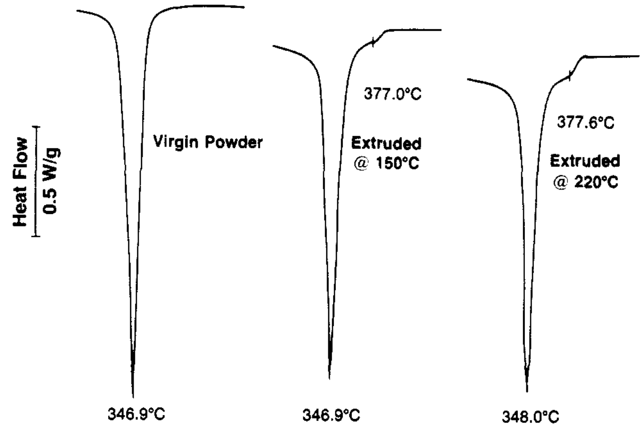


Figure 8. DSC thermograms (10 °C/min) showing the effect of solid state extrusion on the melting behavior of PTFE (sample 6).

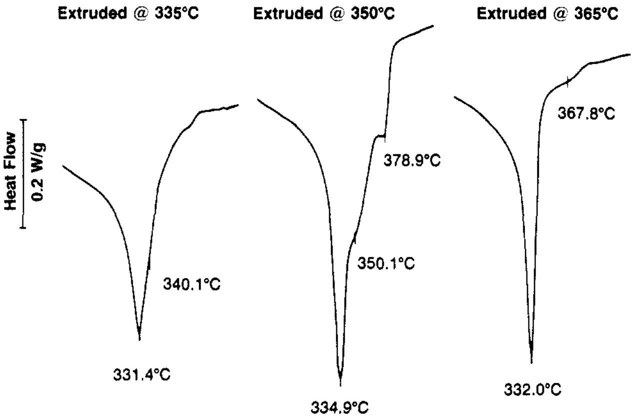


Figure 9. DSC thermograms (10 °C/min) showing the effect of melt-extrusion temperature on the melting behavior of PTFE (sample 6).

An Instron capillary rheometer was used to prepare extrudates of sintered PTFE at various shear rates.

Hot-stage optical microscopy was performed by using a Leitz Ortholux optical microscope equipped with a specimen heating stage capable of maximum temperature of 350 °C. The sample was heated (10 °C/min) and viewed in transmitted light with crossed polarizers. Under these conditions the crystalline nature of the PTFE gives rise to a strong optical birefringence effect that disappears as the crystalline melt temperature is reached.

X-ray diffraction (XRD) patterns were recorded by using a Nicolet area detector mounted on a Huber two-circle horizontal diffractometer. A Mettler DSC cell was used to simultaneously record the DSC scan during the XRD data collection. Nickel-filtered copper radiation and a heating rate of 5 °C/min were used. XRD patterns were recorded at desired tempera-

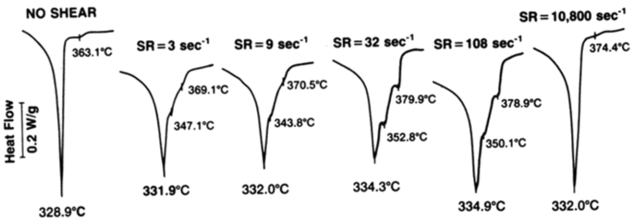


Figure 10. DSC thermograms (10 °C/min) showing the effect of shear rate (SR) at 350 °C on the melting behavior of PTFE (sample 6).

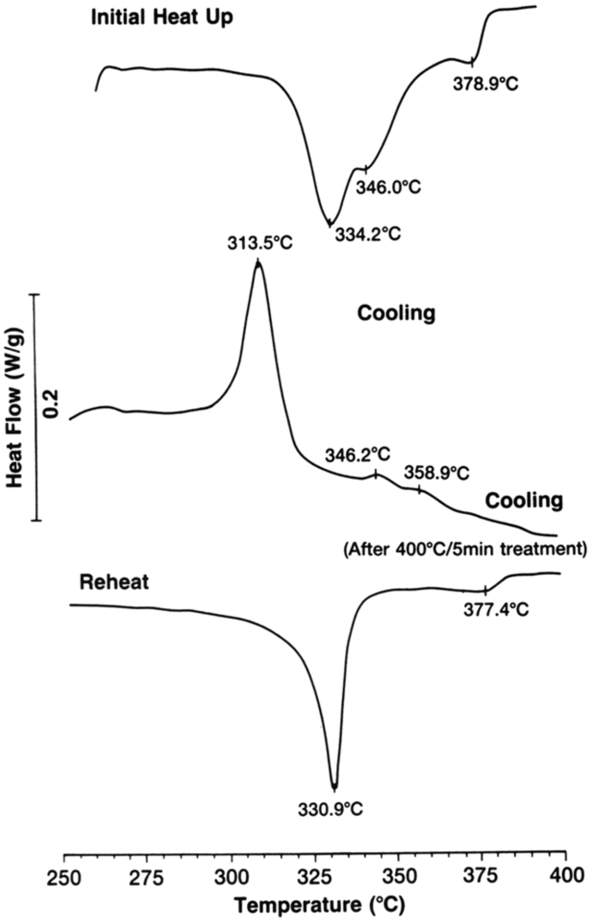


Figure 11. DSC thermograms (10 °C/min) showing the melting, melt-crystallization, and subsequent melting of a sintered PTFE (sample 9).

tures with 1- or 2-min exposure. Some of the XRD patterns were also obtained under isothermal conditions.

Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGS-2 unit in argon atmosphere using ~5 mg sample and a heating rate of 10 °C/min.

Infrared (IR) spectra were obtained by using a Perkin-Elmer Model 983 ratio-recording double-beam dispersive spectrophotometer under resolution conditions of 3.0 at 1000 cm^{-1}. The samples for IR were molded in an aluminum foil package at 340 °C under similar conditions.

Results and Discussion

We have recently suggested that the melting temperature of virgin and sintered PTFE should be nearly the same, $T_m \simeq 330 \pm 3$ °C in the absence of superheating.[5] At commonly used heating rates e.g., 10 °C/min, superheating artificially raises the T_m of virgin PTFE to a value of ~341 °C due to its extended chain morphology as reported in the literature.[3-5] Now we wish to report a new, high-temperature transition ($T_m \simeq 370 \pm 10$ °C) in sintered PTFE which otherwise has been known to exhibit the highest transition (melting) at ≃327 °C at 10 °C/min.

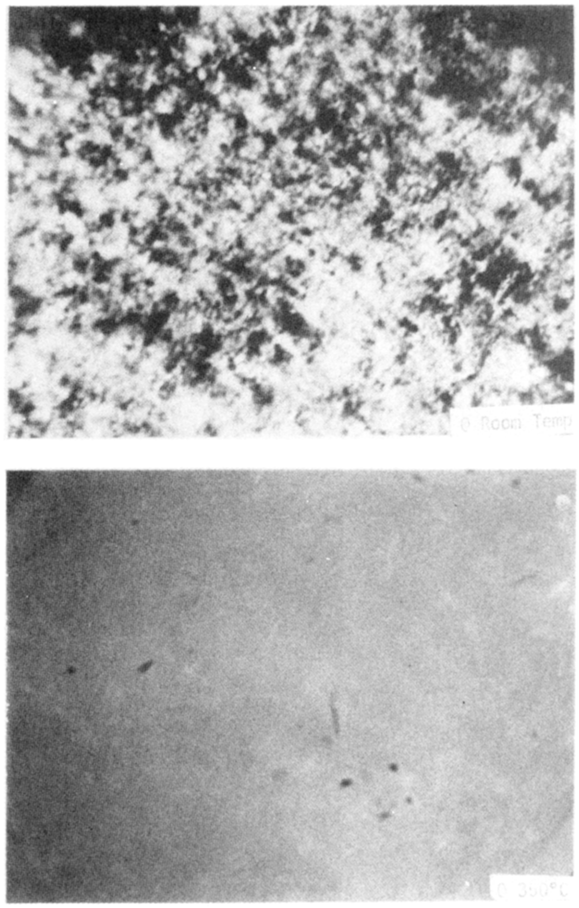


Figure 12. Optical photomicrographs at room temperature and 350 °C of a sintered PTFE which does not exhibit any significant $T_{od} \simeq 370$ °C (sample 1).

Differential Scanning Calorimetry. A sintered block of commercially available PTFE (sample 1) was cut into a disk for use as a reference material in our thermal conductivity apparatus. The disk (sample 1a) had been exposed to complex thermal cycling under moderate pressures during occasional thermal conductivity measurements over a 2-year period. Since sample 1a was considered to be well annealed, we carried out DSC and dynamic mechanical analyses (DMA) and the results were surprising (Figure 1). *Duplicate* runs yielded a $T_m = 370.1 \pm 0.3$ °C and a heat of fusion (ΔH_f) = 8.57 ± 0.03 cal/g for the sample 1a. Interestingly, duplicate runs on the control, sample 1 yielded a $T_m = 331.9 \pm 0.4$ °C and a ΔH_f = 6.85 ± 0.10 cal/g (Figure 2) which is typical of a sintered PTFE. All these experiments were carried out on the same day (August 27, 1986) between 11 a.m. and 3 p.m., and our Perkin-Elmer DSC-2C unit has not been off by more than 1 °C; actually at 11 a.m. on the onset of melting of a tin standard was found to be 231.87 °C while the literature value is quoted to be 231.88 °C. A crystal–crystal transition at 20 °C (Figure 1) and the relaxation pattern (Figure 3) should confirm the identity of sample 1a as PTFE in view of the published literature.[4,6]

Since sample 1a is no longer available, we have tried to modify sample 1 through annealing. Sample 1 itself shows a trace endothermic order → disorder transition (T_{od}) at about 365 °C (Figures 4 and 5). However, thermal annealing of sample 1 over a temperature range of 310–350 °C for a period up to 65 h has not been effective in increasing the intensity of the 365 °C peak. Selective annealing at 325 °C under a pressure of 10–900 atmospheres has also been ineffective. Orientation induced

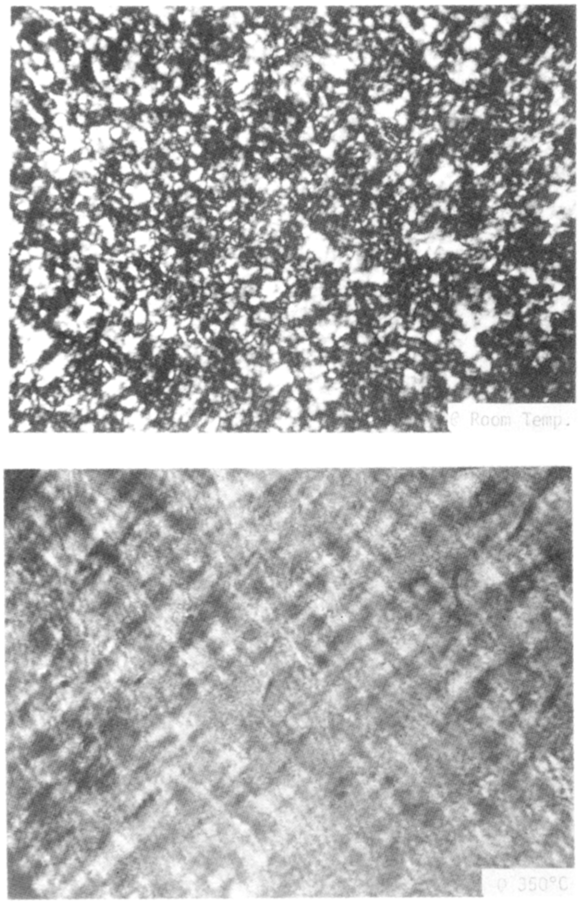


Figure 13. Optical photomicrographs at room temperature and 350 °C of a sintered PTFE which does exhibit any significant $T_{od} \simeq 370$ °C (sample 8).

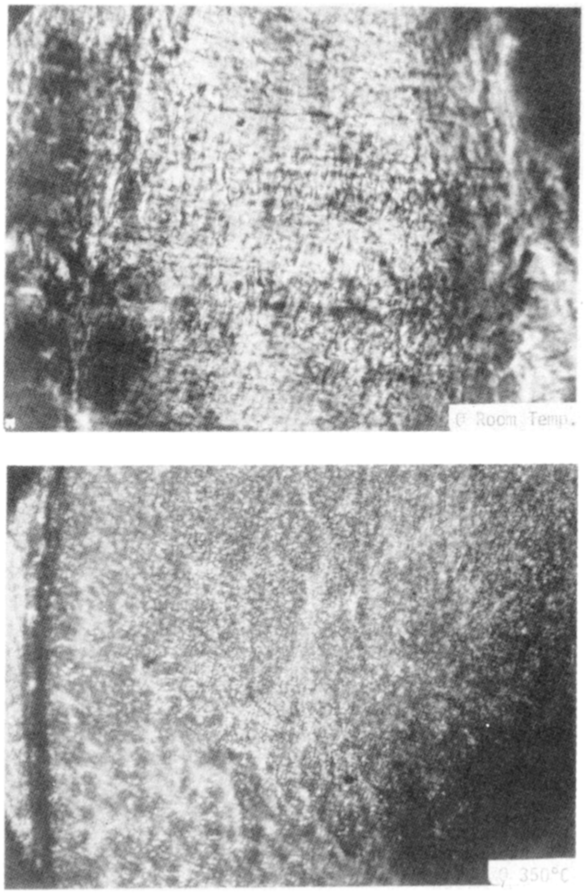


Figure 14. Optical photomicrographs at room temperature and 350 °C of a sintered PTFE which exhibits high-temperature transitions (sample 9).

by stretching at room temperature had no effect either.

Interestingly, a trace peak in the 360–380 °C region has been identified in many samples of PTFE. For example, a commercially sold PTFE tape (sample 2) exhibits a similar transition (Figure 6). We observe that the trace peak at ~365 °C goes parallel with a clearly identifiable exothermic, disorder → order transition (T_{do}) at 346 ± 1 °C upon cooling the melt after a treatment of 380 °C/5 min (Figure 7); sample 3 is a film of PTFE obtained from a source outside the U.S. Analysis of several samples from various sources indicates that the T_{do} at 346 °C (corresponding to the T_{od} at 365 °C) occurs mainly when the molecular weight is high (samples 4–7; Tables II and III). For example, a particular sample exhibiting T_{do} at 346 °C, when degraded by thermal treatment at 450 °C, shows a decrease in molecular weight, and this is accompanied by the loss of T_{do} (Table III). Radiation degraded PTFE does not exhibit the $T_{do} \simeq 346$ °C either.

While the relationship of high molecular weight to the $T_{od} \simeq 370$ °C is indicated by the DSC, the following rheological study will demonstrate the role of moderate shear stresses in the solid ↔ melt region.

Rheological Study. Preliminary extrusion experiments in the temperature range of T_g and T_m using a capillary rheometer introduce the 370 °C transition in a powder which does not have it to start with (Figure 8). It appears that the moderate shear rates, e.g., about 100 s^{-1}, applied at a temperature of about 350 °C are effective in introducing the high-temperature transitions; without shear the PTFE exposed to 350 °C melts at about 330 °C (Figures 9 and 10). It is possible that further optimization efforts can lead to the selective formation of the material with 370 °C ± 10 °C transition morphology. It should be interesting to note that the newly introduced high-temperature transitions can be partially reversible (Figure 11).

Hot-Stage Optical Microscopy. Sintered samples 1 and 8 of PTFE do not exhibit an easily detectable $T_{od} \simeq 370$ °C transition. Optical photomicrograph of sample 1 shows complete loss of birefringence upon heating from room temperature to 350 °C (Figure 12). A trace of birefringence can still be detected in sample 8 at 350 °C, although DSC of this sample cannot detect any major high-temperature transition (Figure 13). Sample 9 with high-temperature transitions (Figure 11), however, exhibits a highly birefringent structure at 350 °C (Figure 14).

Variable-Temperature X-ray Diffraction. X-ray diffraction patterns from PTFE samples without and with the high-temperature transitions are shown in parts a–c and parts d–f, respectively, of Figure 15. These patterns show a sharp equatorial reflection at $2\theta = 18°$ overlayed on an amorphous halo centered at $2\theta = 17°$. Both the crystalline and amorphous peaks shift to lower angles as a result of thermal expansion. More significantly, while the control (sample 8) shows only an amorphous halo at ≈330 °C (Figure 15c), sample 9 shows a crystalline reflection even at 370 °C (Figure 15f). This, along with the DSC scan obtained during the XRD measurements, shows that sample 8 melts at 335 °C, and sample 9 remains crystalline up to 375 °C.

In an XRD pattern of yet another oriented sample which exhibited the 370 °C transition, we were able to observe a layer line reflection at $2\theta = 35°$, and this reflection can be attributed to a helical order. This layer line reflection disappeared at 340 °C, while the equatorial reflection was still visible in the XRD pattern. The equato-

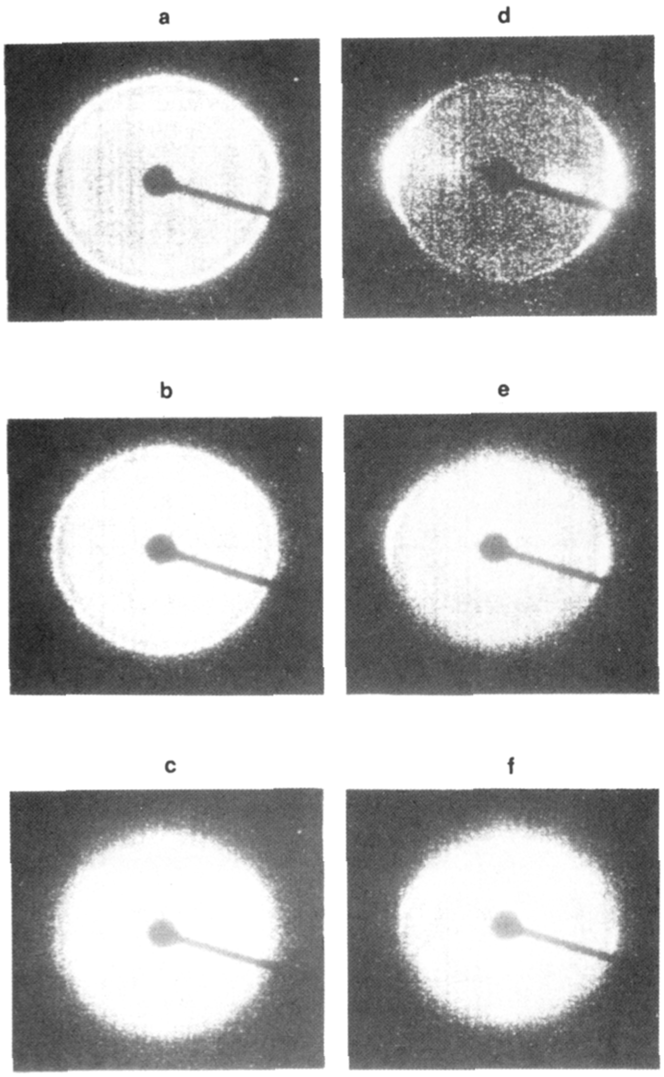


Figure 15. X-ray diffractometer scans of sintered PTFE samples 8 (a, room temperature; b, 300 °C; c, 330 °C) and 9 (a, room temperature; e, 330 °C; f, 370 °C) which show the absence and presence of high-temperature transitions, respectively.

rial reflection disappeared into an amorphous halo at ~360 °C. This can be interpreted as loss of helical order at 340 °C and the persistence of the equatorial order even at 360 °C. Thus, at 335–340 °C three-dimensional order is lost and the T_{od} = 370 °C may be due to the disruption of an equatorially ordered lattice.

Chemical Characterization. TGA thermograms of sample 9 and a reference PTFE (sold by Perkin-Elmer) are similar in degradation characteristics, thus supporting the expected chemical identity of sample 9. It should be interesting to note, however, that the degradation temperature (stability) of sample 9 is about 15 °C higher, probably due to the morphological modification (Figure 16).

Infrared absorbances of sample 9 and a reference PTFE are identical, thus confirming the chemical identity of the subject sample 9 as PTFE (Figure 17). Note that the two samples were remolded at 340 °C in order to obtain films of similar thickness; actually sample 9 is about 15% thicker on the basis of the the 2366 and 205 cm^{-1} absorbances. The remolded sample 9 has a higher crystallinity than the reference, on the basis of the reduced 773, 741, and 720 cm^{-1} absorbances assigned to the amorphous PTFE and the narrower half bandwidths of the major CF_2 absorbances. Detailed morphological analysis of sample 9 by IR would certainly require further work.

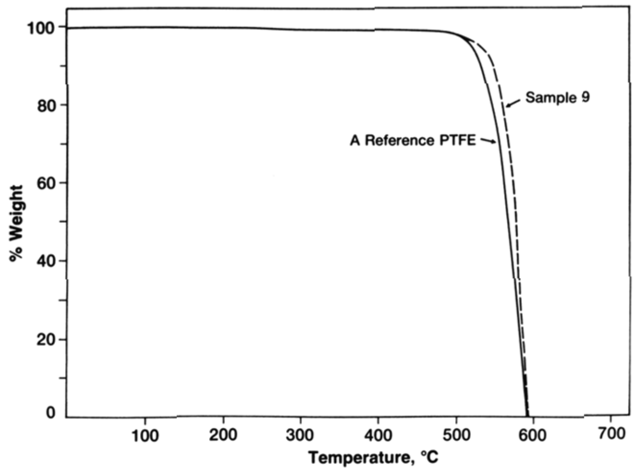


Figure 16. Thermogravimetric analysis curves of sample 9 and a standard PTFE.

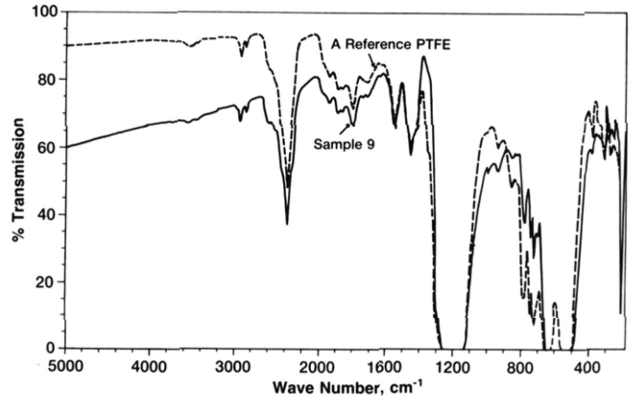


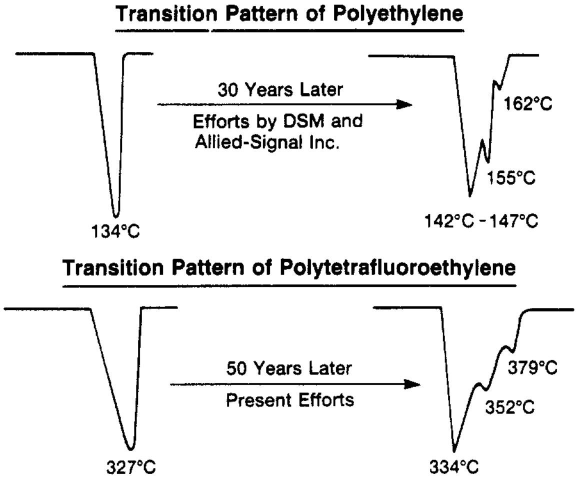
Figure 17. Infrared spectra of sample 9 and a standard PTFE.

Hypothesis for the 370 °C Transition

Regarding the origin of the 370 °C transition, we have no clear explanation at present. On the basis of our experience, the high-temperature transition(s) could be a trace (Figure 4), significant fraction (Figure 11), or even the only transition (Figure 1), depending on the PTFE sample. The 370 °C transition is not due to any superheating effects since it remains intact upon exposures at 350 °C during the optical microscopy and X-ray diffraction measurements, and especially upon 400 °C/5 min treatment in the DSC (Figure 11). On the basis of the XRD study we believe that the 330 °C transition represents the loss of helical order while the 370 °C transition may be associated with the disruption of the remaining two-dimensional structure, i.e., equatorial order. We hypothesize that the stability of the two-dimensionally ordered lattice, i.e., intensity of the 370 °C transition is dictated by shear-induced molecular constraints (e.g., through tie molecules or entanglements) on the crystals. Such constraints are cited as the key to the formation of unusually high-temperature transitions in polyethylene.[7] Molecular constraints created by moderate shear rates in the solid ↔ melt region would be favorable in high molecular weight samples, and this will explain the loss of the 370 °C transition when the molecular weight is reduced by irradiation or thermal degradation. As this is the first report on the observation of high-temperature transitions in PTFE, further XRD and spectroscopic studies are needed to better understand the phenomenon.

Significance of This Work

The scientific and perhaps practical value of this study can be appreciated when considering the analogy between polyethylene and PTFE where processing developments over the decades have led to unusually high temperature transitions. This implies that other common polymers may also yield new morphologies representing novel properties.



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Thermodynamics of the Aggregation Phenomenon in Associating Polymer Solutions[†]

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ABSTRACT: The effect of temperature on the extent of aggregation, in dilute solution, of sodium sulfonated polystyrene ionomers in xylene has been determined by using small-angle neutron scattering (SANS). The data are described by using the open association model in which it is assumed that an equilibrium is eventually formed between single chains and aggregates of all sizes. The extent of aggregation was found to be temperature independent which suggests that there is no change in enthalpy on forming aggregates. It was therefore suggested that on aggregation intramolecular ion pair associations are broken and the same number of intermolecular associations formed. Intramolecular ion pair associations in the ionomer solutions were shown to collapse the single-chain radius of gyration (R_g) at infinite dilution to a value less than half the single chain dimension of normal polystyrene in this solvent and also smaller than for polystyrene in Θ solvents. The temperature dependence of the second virial coefficient for the ionomers was determined and compared with values for polystyrene. It was also found that 2% by volume of methanol was enough to almost completely solvate all the ionic groups and prevent both inter- and intramolecular ion pair associations in dilute solution.

Introduction

Ionomers are macromolecules containing a small number (typically less than 10 mol %) of ionic groups chemically attached to a nonpolar backbone. These materials have been commercially available for many years as modified thermoplastics and elastomers. Until very recently relatively little work had been published on their dilute solution behavior. It was suggested that one reason for this lack was due to the limited solubility of these commercially available ionomer polymers.[1] Within the last few years, however, the properties of sulfonated polystyrene ionomers in the polar solvents dimethyl sulfoxide[2] and dimethylformamide[2-4] and the nonpolar solvents xylene[5,6] and tetrahydrofuran (THF)[7,8] have been studied. It was shown that in polar solvents the iono-

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[†] This paper is dedicated in honor of the 60th birthday of Professor Walther Burchard of the Institut für Makromolekulare Chemie, Freiburg. We have many happy memories of discussion with Professor Burchard and hope for many more in the future.

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