Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer 45 (2004) 2031–2039

polymer

www.elsevier.com/locate/polymer

Melting and crystallization behavior of poly(tetrafluoroethylene) by temperature modulated calorimetry

Rachele Pucciariello*, Vincenzo Villani

Dipartimento di Chimica, Università della Basilicata, Via N. Sauro 85, 85100 Potenza, Italy

Received 10 August 2003; received in revised form 12 December 2003; accepted 18 December 2003

Abstract

Temperature-modulated differential scanning calorimetry (TMDSC) in the quasi-isothermal mode is applied to investigate melting and crystallization of poly(tetrafluoroethylene) (PTFE) obtained from aqueous dispersion, both melt-crystallized and native (as-polymerized). The differences, shown in the past between the melting behavior of melt-crystallized and native PTFE, have been confirmed and further evidenced through this technique. A large reversing heat capacity is present in the melting and crystallization regions. As proposed by many authors, the presence of the reversing heat capacity can be related to surface melting and crystallization. It can occur on the growth and/or fold surfaces and it has been shown that it is larger for those macromolecules having higher chain mobility that allows rearrangements on the crystal surface. In the present case, the large observed reversing heat capacity can be related to the very high sliding ability of PTFE chains in the pseudohexagonal phase, which is much larger than that of most semicrystalline polymers. Due to the crystal–crystal transition at 30 °C, which can be described as a fusion in the longitudinal direction, melting of PTFE can be considered intermediate between the irreversible melting of macromolecules and the completely reversible isotropization of liquid crystalline polymers.

Keywords: Poly(tetrafluoroethylene); Reversible melting; Temperature modulated calorimetry

1. Introduction

Melting and crystallization of polymers are well known to be irreversible because of the metastability of the macromolecular crystals, of the need of supercooling, due, in turn to the need for primary nucleation and of the necessity of molecular nucleation before a macromolecule can add itself to a crystal [1]. All these features cause that, given a temperature, equilibrium crystals and melt do not coexist.

Very recently, the development of the temperature modulated differential scanning calorimetry (TMDSC) opened new perspectives on a series of phenomena and in particular on polymer melting and crystallization ([2–10], for example).

In TMDSC the common temperature program is superimposed with a dynamic temperature change (sinusoidal or saw-tooth) with an frequency $\omega = 2\pi/p$ (where p is the period) and an amplitude A_t, according to (for the sinusoidal case):

$$T(t) = T_o + \beta_o t + A_t \sin \omega t$$

The thermal response, i.e. the recorded heat flow $\Phi(t)$ is separated into an underlying (static) heat flow (nearly corresponding to the conventional DSC curve) and into a dynamic (complex, frequency-dependent) component. The modulus of the complex heat capacity, the so-called reversing component of the heat flow is calculated through the Fourier analysis of the measured signal from the amplitude of the first harmonic of the Fourier series. The reversing component represents the thermal response that is recovered in one period of the temperature modulation.

Many authors have found clear evidence of relation between the reversing heat capacity and reversible processes in melting and crystallization of macromolecules. Albrecht et al. [2,3] showed that polymers with a high longitudinal diffuse mobility within the crystallites give reversible surface melting and crystallization. Goderis et al. [5] evidenced in linear polyethylene reversible processes occurring at an active surface of the lamellar crystals, in particular the fold surface. The authors related the presence

---

* Corresponding author. Tel.: +39-0971-202227; fax: +39-0971-202223.

E-mail address: pucciariello@unibas.it (R. Pucciariello).

0032-3861/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2004.01.019

of reversible melting to the ability of the chains to undergo sliding diffusion within the crystals. In fact, the reversible melting occurs for poly(ethylene) or poly(ethylene-oxide), which are known to present sliding of their chains within the crystals, it reduces for poly(ethyleneterephtalate), poly-(ϵ-caprolactone) and isotactic poly(propylene) and is completely absent in syndiotactic poly(propylene), according to the more and more reduced sliding ability. Schick and coworkers [7–9] interpret the occurrence of reversible melting as due to equilibrium between the surfaces (growth and/or fold) of the individual crystallites and the surrounding melt. By means of a very impressive expression they define polymer crystals as 'living crystals'. Schimdtke et al. [10] showed that reversible contributions to the heat capacity in the melting range occurred in polymers such as syndiotactic polypropylene without surface melting and were attributed to melting and crystallization processes occurring at small supercooling and superheating.

The above studies concern relatively perfect, lamellar crystals of highly crystalline samples. Other authors showed that the reversible events are more evident in more defective and thinner crystals, where, as reported by Androsch et al. [4], the reversibility originates from melted portions of the chains, which, being joined to higher melting crystals (that are still in the solid state) can be reattracted undergoing again crystallization, during the reduction of temperature performed during the modulation range. In fact, due to their metastability, polymer crystals melt at temperatures that are below the equilibrium melting temperature, where crystal growth is still possible.

The melting behavior of PTFE, differing in many aspect with respect to most synthetic polymers, has often been investigated by conventional differential scanning calorimetry (DSC). A double melting peak has been observed for the native polymer, when obtained from aqueous dispersion polymerization, while only one is observed for the melt-crystallized polymer, at lower temperature and with a lower enthalpy of fusion [11]. Various interpretations have been suggested for this peculiar behavior. In particular, Rahl et al. [12] showed that native PTFE presents a folded ribbon morphology, where the lamellae fold a number of times on themselves. Electron diffraction showed that the ribbons are single crystals with the chain axis parallel to the long axis of the ribbons. Then, in the folded ribbons, linear and folded regions coexist. In contrast, for the melt-crystallized polymer, an extended chain morphology has been shown, where the crystalline regions are connected one to the other through amorphous ones. The longitudinal dimensions of the crystallites are similar in the ribbons, and in the extended chain crystals, in contrast the lateral dimensions of the ribbons are much greater than those of the extended chain crystals. In contrast, Bassett, through the application of the kinetic theory of folded chain crystallization to PTFE, showed that PTFE does not represent a special case, but can be considered a folded chain polymer whose lamellar thickness is much higher than that of most polymers [13]. Suwa et al. [14], on the basis of the morphology proposed for native and melt-crystallized PTFE, elaborated a model, explaining the experimental findings concerning the melting behavior of PTFE as follows. The double melting pattern of the native sample is due to the melting of the folded regions (low temperature) and linear regions (high temperature) coexisting in the folded ribbons. The lower melting temperature of the melt-crystallized crystals is due to their smaller lateral dimensions with respect to that of the native crystals. The lower enthalpy of fusion of melt-crystallized PTFE is due, as it is well-known, to the low molecular mobility of PTFE in the molten state, which, in turn is ascribed to its very high melt viscosity [15].

In this paper, we perform a series of temperature-modulated DSC measurements in the quasi-isothermal mode, for melting and crystallization of both melt-crystallized and native PTFE. Our aim is to get more insight into the nature of these phenomena, to eventually find processes that are not visible through conventional DSC, which may be able to clarify the peculiar melting behavior of PTFE and the difference between the native and the melt-crystallized sample. We find the presence of a large excess reversing heat capacity in the melting and crystallization regions. The excess reversing heat capacity may be related to reversibile events occurring at the surface of PTFE crystallites and can be connected to the very high sliding abiltity of the PTFE chains in the crystal. Such high mobility is due to the presence of the hexagonal to pseudohexagonal transition at 30 °C. In fact, we remind that in the phase stable from 30 °C up to the melting point the lateral order is mantained, but the longitudinal one is lost, as evidenced many years ago by Bunn and Howells [16]. Starkweather, through rheological experiments, showed that this phase is mesophase-like, in particular the rheological behavior of PTFE up to 300 °C is similar to that of low-molecular weight smectic states [17].

2. Experimental

2.1. Materials

A commercially available powder sample of PTFE has been used throughout this work. It was obtained by dispersion aqueous polymerization. The dispersion was coagulated by mechanical stirring, then washed and dried under vacuum. The molecular weight, $\overline{M}_\mathrm{n}$, was evaluated according to the Suwa et al.'s empirically derived relationship between the number average molecular weight and the heat of crystallization [14]

$$\overline{M}_\mathrm{n} = 2.1 \times 10^{10}\ \Delta H_\mathrm{c}^{-5.16}$$

and was estimated as about 8×10^5 g/mol

The crystallinity of the samples was evaluated through differential scanning calorimetry (see below) as

$$\Delta H_\mathrm{m}/\Delta H_\mathrm{m}^\mathrm{o}$$

where ΔH_m is the measured heat of fusion and ΔH_m^o is the heat of fusion of a perfect crystal of PTFE [18].

For the native sample a calorimetric crystallinity index $I_{DSC} = 0.90$ was obtained, for the sample crystallized from the melt (heated at 10 °C/min up to 400 °C, then cooled to room temperature at the same scanning rate) $I_{DSC} = 0.37$.

2.2. Instrumentation

The TMDSC measurements were carried out on a Perkin Elmer DSC7 in the DDSC quasi-isothermal mode.

The sample temperature T was set at a fixed mean temperature T_o plus a small periodic, saw-tooth perturbation with a frequency ω ($\omega = 2\pi/p$, where p is the period) and an amplitude A_t according to:

$$T = T_o + A_t \times 4/\pi(\sin \omega t/1 - \sin 3\omega t/9 + \sin 5\omega t/25 - \ldots)$$

A_t is set as 0.5 °C, while for p the following values have been used: 20, 30, 60, 100 and 200 s (corresponding to 0.21, 0.31, 0.11, 0.063, 0.031 mHz, respectively).

To let the measurement cover the whole melting range, the mean temperature was increased or decreased by stepwise changes of 2 °C after each quasi-isothermal treatment to construct a heating or a cooling process, respectively. The quasi-isothermal runs lasted 10 min for each temperature. The heat capacity data of the last 5 min were averaged and taken as the data point for the given T_o.

The recorded heat flow $\Phi(t)$ is analyzed using the complex heat capacity approach by Schawe [19], which allows to obtain the dynamic component as a complex, frequency-dependent function, whose modulus is the reversing heat flow [20], i.e.

$$|c(T,\omega)| = \frac{\Phi_a(T,\omega)}{A_t\omega}$$

where Φ_a is the amplitude of the dynamic component of the heat flow.

The crystallinity w_c was calculated by dividing the integral of the peak, obtained by heating the sample after each quasi-isothermal step in the conventional DSC mode, by ΔH_o, the reference transition enthalpy of PTFE (82 J/g) [18]. Using these calculated crystallinities the base line heat capacity, or the thermodynamic heat capacity $C_{pb} = w_c C_{pc}(T) + (1 - w_c)C_{pa}(T)$ is calculated, where C_{pc} and C_{pa} are the reference heat capacities of crystalline and amorphous material, respectively, taken from the ATHAS databank [18]. In the figures shown in the next section we report the apparent reversing heat capacities together with the so-calculated C_{pb}, in order to evidence the difference between the apparent reversing heat capacity and C_{pb}, and have an indication of the true excess contribution that may be related to reversible phase changes.

Temperature calibration was done in the standard DSC mode using the onset melting temperatures of indium and zinc and the heat flow rate calibration was realized using the heat of fusion of indium at a scanning rate of 10 °C/min.

The transition temperatures have been taken as those corresponding to the maxima of the peaks and their uncertainty is ±0.3 °C. The measurements were performed on 5 ± 0.5 mg samples, anyway we have verified that our results do not depend on the sample mass. Nitrogen was purged into the cells.

The measurements which refer to melt-crystallized samples, mean samples that have been taken to 400 °C at a heating rate of 10 °C/min, hold at this temperature for 10 min, then cooled to room temperature at the same rate. The measurements concerning the native sample, indicate samples which have never been subjected to thermal treatments (as-polymerized).

The used instrumentation has been demonstrated to be a linear system, therefore suitable to dynamic measurements [21].

3. Results and discussion

We have evaluated the dynamic heat capacity for PTFE in quasi-isothermal experiments. The mean temperature, being changed step for step, was varied through the whole melting (or crystallization) range of the sample. The modulation period was varied in the range from 20 to 200 s, as reported in Section 2.

Due to the different behavior of melt-crystallized and native PTFE, we will discuss them separately, starting from the first one.

As above described in all the figures reporting the apparent reversing heat capacity, also the thermodynamic heat capacity is shown, in order to read, from the difference between the first and the second, the excess heat capacity, due to reversible melting and crystallization.

Fig. 1 shows the reversing heat capacity measured during the melting process of melt-crystallized PTFE upon increasing the period from 20 to 200 s. At each modulation period a large reversing heat capacity is observed in the melting range. The signal in the melting region is always strong with a maximum in the melting range.

In Fig. 2 the temperature corresponding the maximum of the signal, namely T_m, is reported, resulting independent upon the modulation period.

In Fig. 3 the reversing heat capacity obtained during the cooling process from the melt state is depicted. Also in this process a large reversing heat capacity is recorded during the formation of the crystals, showing always a maximum in the crystallization region. A supercooling of about 10 °C is observed. The occurrence of supercooling is in agreement with the formation of macromolecular crystals, that, as said above, requires nucleation [1]. Moreover, as reported in Fig. 2, the peak temperature remains constant, independently upon the modulation period.

As said above, the melting behavior of native PTFE from aqueous dispersion polymerization has been in-depth studied in the past by conventional DSC [11,22–25]. In particular, Starkweather [11] studied the effect of the

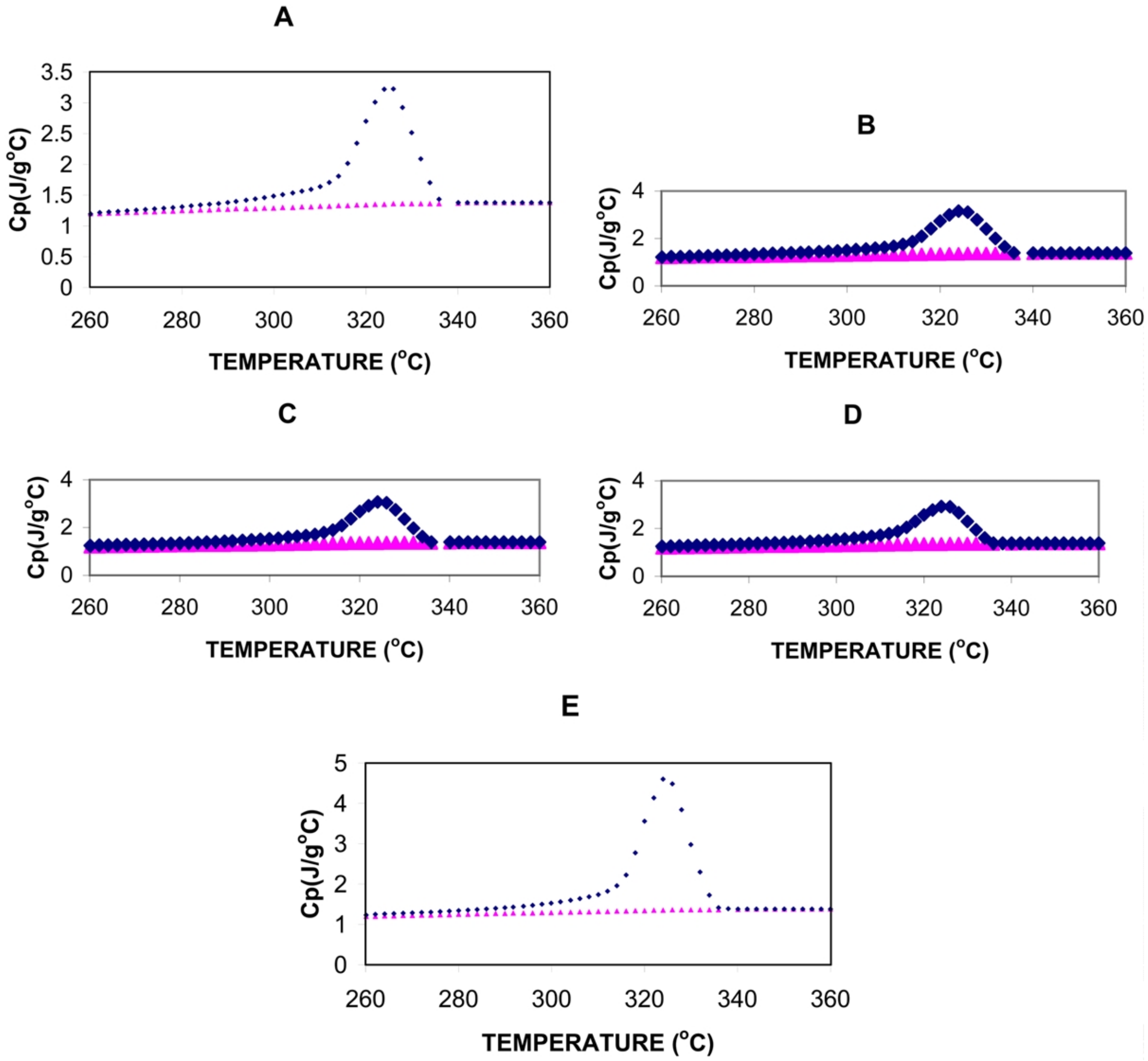

Fig. 1. Quasi-isothermal TMDSC measurement for melt-crystallized PTFE (taken to 400 °C at 10 °C/min, hold at this temperature for 10 min, then cooled to room-temperature at 10 °C/min), in the heating process (◆) and calculated baseline heat capacity (▲). (A) 200 s, (B) 100 s, (C) 60 s, (D) 30 s, (E) 20 s.

heating rate on the melting of native PTFE. He found that for very high scanning rates (50 °C/min) one melting peak is present, on decreasing the scanning rate a shoulder at lower temperatures appears, which prevails on further decreasing the scanning rate (at 2 °C/min). Moreover, the two peaks undergo superheating, i.e. the peak temperatures increase on increasing the heating rate. In previous papers [22–25], we have in-depth examined this phenomenon, and, on the basis of DSC and X-ray diffraction studies interpreted these data by taking into account the morphology proposed by Rahl et al. [12] for native PTFE, attributing the lower of the two melting peaks to the folded regions and the higher to the linear segments of the folded ribbons.

In Fig. 4 we report the reversing heat capacity recorded on heating the native sample. Also in this case a large reversing heat capacity is attained with a maximum in correspondence of the melting range. Anyway, as already observed by conventional DSC, the behavior of the native sample differs from that of the melt crystallized one under many aspects. The temperature corresponding to the maximum is much higher than that recorded for the melt-crystallized sample (at least 10 °C above), as observed by DSC; moreover, in contrast to melt-crystallized PTFE, where, independently upon the frequency, the maximum is located at about the same temperature (around 324 °C), here it moves towards higher temperatures on decreasing the modulation period. Also the shape of the curve is different: at the modulation period of 60 s a shoulder at higher temperatures appears at about 340 °C, which becomes more and more evident for shorter periods. In fact, it becomes the main peak for periods of 30 and 20 s. The superheating, increasing on faster modulations, is clearly evident from Fig. 2(B), where the peak temperatures as a function of the modulation period are reported. The described behavior reminds what obtained by Starkweather. In particular, we note that the results obtained on fast modulation (high frequency) correspond to those recorded on high scanning rates (up to 20 °C/min). Moreover, superheating is observed

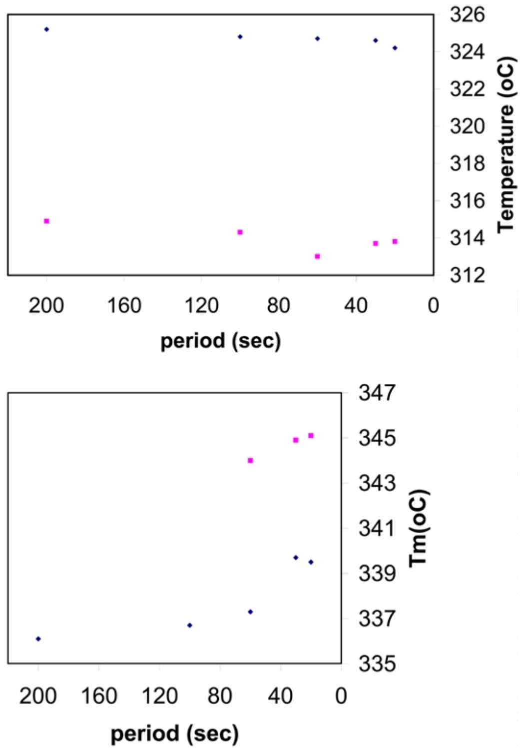

Fig. 2. Transition temperatures as a function of the modulation period recorded in the quasi-isothermal measurements. A: (◆) peak temperature recorded in the heating experiment on melt-crystallized PTFE; (■) peak temperature recorded in the cooling experiment, B: Peak temperatures recorded in the heating experiment on native PTFE.

for both peaks (i.e. on fast modulation the transition peaks shift to higher temperatures) indicating that the melting kinetics is the controlling rate of the transition. This behavior is in agreement with the extended chain character of PTFE crystals: in fact, it has been shown in the past that crystals of flexible macromolecules superheat only when their chains are extended or restrained [1]. Nevertheless, the superheating is higher ($T_m \approx T_m^o + 10$ °C, where the equilibrium melting temperature T_m^o has been evaluated in the range from 332 to 336 °C by several authors [13,26,27]) for the high-melting fraction, while it is much lower ($T_m = T_m^o$) for the low-melting one, in particular for modulation of the order of 200 s. Moreover, let us remember that melt-crystallized PTFE presents the usual melting behavior of folded chain polymers, i.e. $T_m < T_m^o$.

The peculiar trend of the melting temperature of the low-melting fraction of native PTFE, for slow periods of the temperature modulation, seems to approximate the ideal thermodynamic behavior of the polymer, as it can be evidenced by the traditional methods of the determination of the equilibrium melting temperature.

Many authors have attributed the occurrence of the reversing heat capacity in the melting range of macromolecules to surface melting, where the surface can be the growth front and/or the fold surface. In particular the reversible effects at melting have been explained by Schick and coworkers [7–9] considering that, due to the chain structure, a molecule may be at the same time part of the crystal and of the melt. The excess heat capacity observed in TMDSC measurements have been attributed to a latent heat, occurring as a consequence of the possibility of attaching and detaching chain segments during temperature modulation. Another way of explaining the excess heat capacity, proposed by the same authors, is to assume fluctuations around the ‘local equilibrium’ of the chain segments. Such fluctuations generate an entropy fluctuation that can be revealed as the entropy compliance (heat capacity) by means of TMDSC [7–9,28]. The process of reversible melting and crystallization occurs only when high chain mobility exists within the crystallites. In fact, only in that case the chains can slide, giving rearrangements of the involved surface. During the heating segment, the chains on a particular surface, through the sliding diffusion, melt because of the recovery force, due, in turn, to the entangled amorphous regions. During the cooling segment the process is reversed, i.e. surface crystallization takes place [2,3].

The connections between reversible effects and the ability of the chains in the crystals to carry out sliding diffusion have been evidenced by many authors [2,6]. For example, for poly(ethylene) and poly(ethyleneoxide) which are well known to undergo sliding diffusion in the crystals, a large reversing heat capacity is observed in the melting range (C_p(maximum)/C_p(melt) > 1.2). In contrast, when the longitudinal mobility in the crystals is much reduced or completely absent, such as in poly(ethyleneterephtalate), poly(ϵ-caprolactone), isotactic poly(propylene), syndiotactic poly(propylene), only a small or no reversing heat capacity is observed [2,3].

In Fig. 5 we report the ratio of C_p(maximum)/C_p(melt) for the heating measurements of native and melt crystallized PTFE and for the cooling from the melt state, as a function of the applied modulation period. It is apparent that the ratio C_p(maximum)/C_p(melt) is for PTFE much larger (always greater than 2.0) than the values reported in the literature for the other polymers characterized by high sliding ability. Moreover, PTFE is well known to possess exceptional frictional properties that are due to the movements of the polymer molecules parallel to their axes. In fact, PTFE presents, close to room temperature, two crystal–crystal transitions [16,29,30]. At low temperatures (below 19 °C) PTFE gives a well-ordered triclinic structure, which at such a temperature develops some disorder which arises from a mechanism that rotates the atoms about the molecular axis, but that keeps the molecular axis itself unchanged. At 30 °C the hexagonal cell dimensions and the molecular disorder increases. The main mechanisms of rotation, which have been proposed are the introduction of zig-zag planar sequences and reversals of the hand of the helical molecules. A small rotation of a helical monomer unit can convert it to a planar unit; a larger rotation can reverse the helical sense of the unit. The intramolecular energy necessary to cause the zig-zag planar sequences and the helix reversals in a chain is small in comparison with the thermal energy RT at room-temperature. The pseudohexagonal phase, stable above 30 °C and up to the

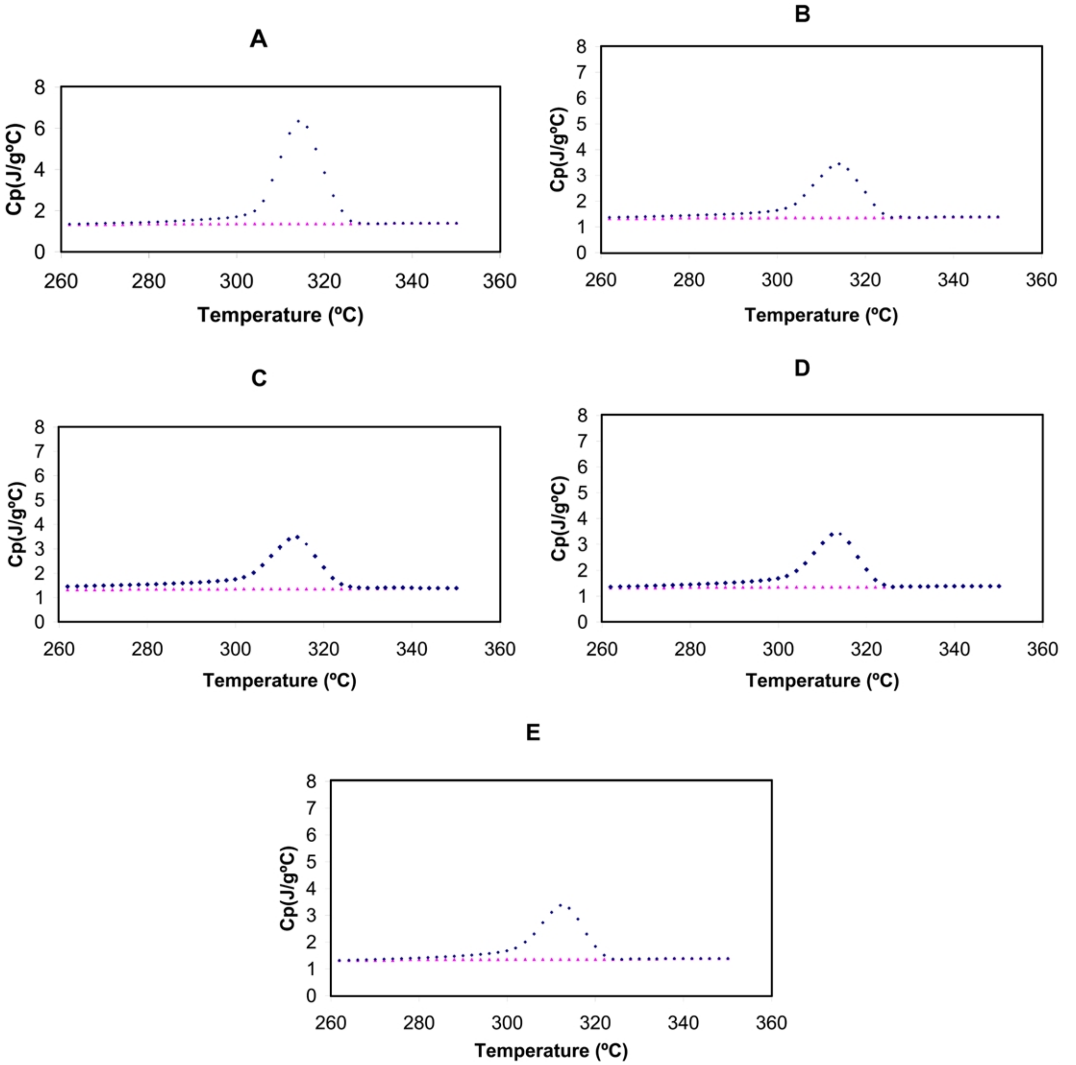

Fig. 3. Quasi-isothermal TMDSC measurement on PTFE in the cooling process from the melt state (◆) and calculated baseline heat capacity (▲). (A) 200 s, (B) 100 s, (C) 60 s, (D) 30 s, (E) 20 s.

melting point (335 °C) the is characterized by dynamic conformational disorder and long-range positional and orientational order, common in liquid crystalline polymers. This phase can be considered as a special kind of mesophase: in fact, the chains maintain their parallelism in a pseudohexagonal array, although they lack a strict periodic correlation in the atomic positions and their conformation corresponds to a disordered succession of helical stretches having opposite sense of spiralization. In this phase the chains experience a large longitudinal mobility, which has compared by Starkweather to that of a smectic liquid crystal [17]. In fact, the author showed that the rheological behavior of PTFE up to 300 °C is similar to that of low-molecular weight smectic states. In these last ones flow occurs along planes normal to the long axes of the molecules. In the pseudohexagonal phase of PTFE flow occurs along planes parallel to the chain axes.

On the basis of the above considerations we suggest that the transition at 30 °C presents the character of a longitudinal fusion along the chain axis, therefore it can be classified as similar to that from an ordered crystal to a smectic-like liquid crystal.

In a previous paper [31] we have analyzed in depth the low-temperature behavior of PTFE by TMDSC in the scanning mode (i.e. $\beta_o \neq 0$), in order to evaluate the frequency dependence of heat capacity which, in turn, gives information on the time dependence of the structural changes involved in the transformation. We analyzed the dynamic component of the heat flow through the Schawe method [19], i.e. evaluating the two components of the complex modulus c' and c'', called storage and loss component, respectively. We found that the pseudohexagonal to hexagonal transition does not require supercooling, while the hexagonal to triclinic one does; the trend of the storage and loss components of the heat capacity also indicates a higher reversibility for the pseudohexagonal transition than for the hexagonal to triclinic one.

Due to the crystal-disordering transition, melting of PTFE shows similarities to the isotropization of polymeric liquid crystals. Few years ago, Chen et al. [32] showed that

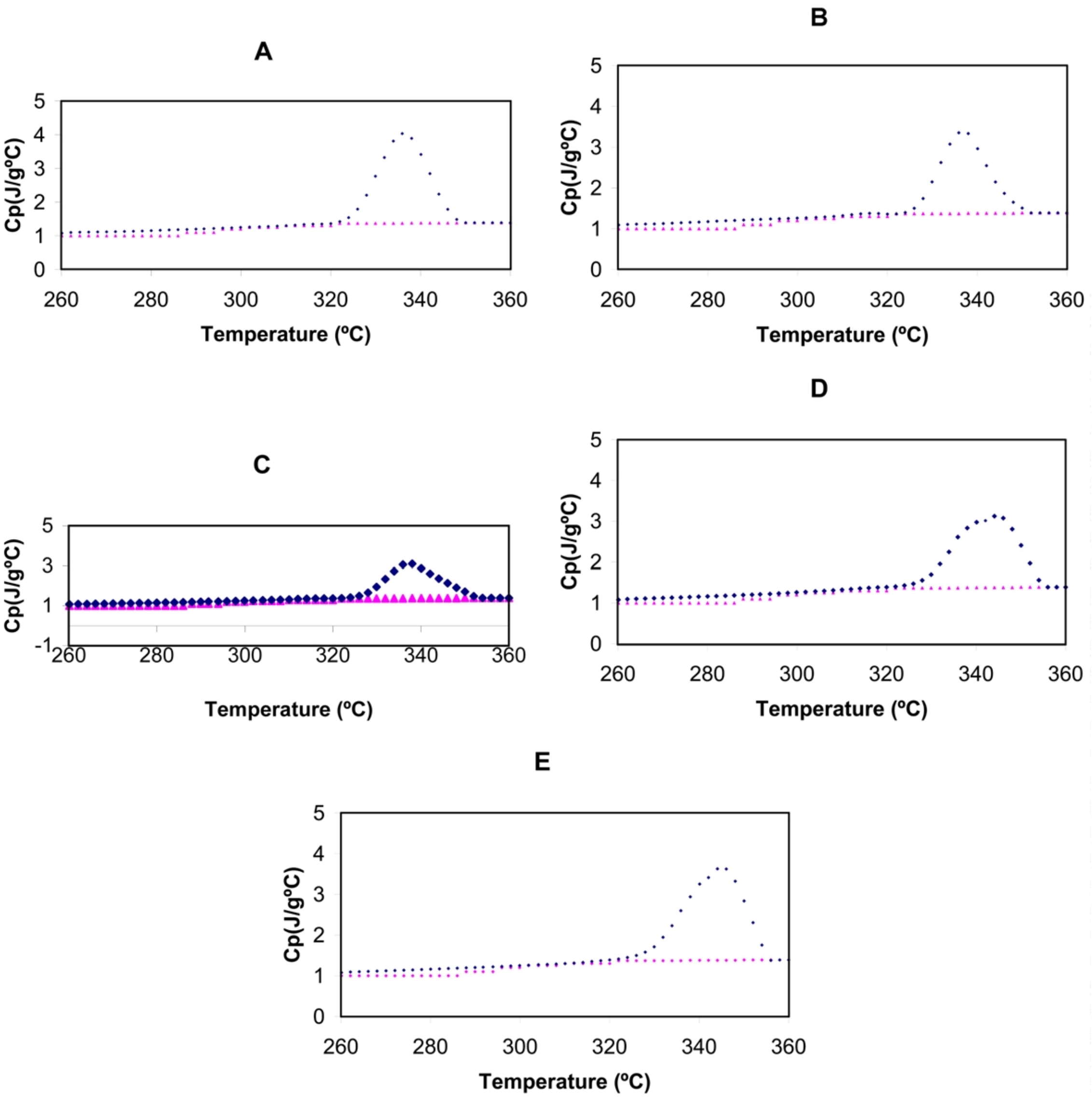

Fig. 4. Quasi-isothermal TMDSC measurement on native PTFE from aqueous dispersion polymerization. Heating process (◆) and calculated baseline heat capacity (▲). (A) 200 s, (B) 100 s, (C) 60 s, (D) 30 s, (E) 20 s.

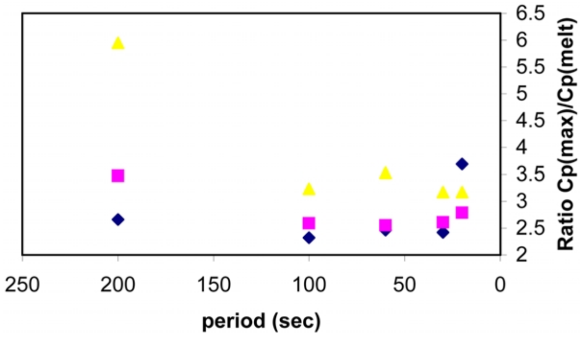

Fig. 5. Ratio of the reversing heat capacity (maximum) of PTFE to that of the melt state (380 °C) for various periods of the temperature modulation. (◆): cooling experiment, (■): heating experiment (native sample), (▲): heating experiment (melt-crystallized sample).

the isotropization of a liquid crystal is thermodynamically reversible, without any supercooling in the ordering process. In contrast, melting of a conformationally disordered (condis) crystal (in particular, a macromolecule containing rigid aromatic segments and flexible aliphatic spacers) is completely irreversible: quasi-isothermal TMDSC traces do not show any contribution in the reversing heat capacity, moreover the crystallization present a 15 °C supercooling. In our opinion the behavior of PTFE is intermediate between the completely reversible isotropization of a liquid crystal and the completely irreversible melting of a condis one. In fact, the supercooling typical for irreversible (nucleation requiring) crystallization occurs; in contrast a large reversing heat capacity is obtained in the melting range, due to the high longitudinal mobility of PTFE chains, due in turn to the transition (partial, longitudinal fusion) occurring at 30 °C. Likely, the longitudinal motions active in the pseudohexagonal phase are reduced because of the high involved molecular weights and the subsequent relevant molecular interactions. Therefore, we define this peculiar state intermediate between the liquid crystalline and the conformationally disordered polymer as soft crystal, similarly to the soft matter defined by de Gennes for a large variety of complex materials, included the macromolecular ones [33].

Also the ordering transition, although requiring supercooling (even if less than for most macromolecules), presents a partial character of reversibility since it is the transition from the melt to a disordered (smectic-like) crystal and not to a well-ordered crystal.

Lastly, we have attempted to obtain information about the dynamics of the observed processes, i.e. to determine the characteristic times associated to them. The oscillating part of the heat capacity depends upon all the internal degrees of freedom of the samples [34]. During the experiment, for example during heating, the sample needs time to absorb the heat needed by all the internal degrees of freedom. Such time is characteristic of the molecular process under consideration. In the simplest case one can consider a simple retardation (relaxation) process that is related to the internal entropy fluctuations. The time depends on the temperature, although its exact dependence is not known. Some authors [35] have proposed for example an Arrhenius behavior. In order to get an insight to time required by the system to establish local equilibrium at the surface of PTFE crystals let us come back to Figs. 1, 3 and 4, where the frequency dependence of the excess heat capacity is reported. Due to the dependence of the relaxation time upon temperature, we have to refer to a specific temperature. In the following we will refer to temperature corresponding to the maximum in the curve of the reversing heat capacity. In Fig. 1 it is evident that the reversing heat capacity for the melting of melt-crystallized PTFE is strongly frequency dependent. At least in the considered time scale, the signal is maximum for the fastest modulation at $p = 20$ s. Then, for $p = 30$ s it decreases to about half of the original value, then it becomes frequency independent. This behavior suggests that the characteristic time associated to surface melting of melt-crystallized PTFE may corresponds to 30 s (i.e. the time when the signal becomes half of its maximum value) and refers to 325 °C.

As well as for the melting of the melt-crystallized sample also for the cooling process not only a strong signal with a maximum is obtained in the crystallization range but also a strong frequency dependence. In particular, the extent of the signal is maximum for the slowest modulation, $p = 200$ s, it decreases to about half of its value for a period of 100 s, then it remains constant on further decreasing the modulation period up to 20 s. This behavior may suggest that the characteristic time associated to the surface ordering process could be localized close to 100 s at 314 °C. The reorganization of the crystallites is, anywhere, as well as melting, a complex process, that cannot be represented by a single relaxation process, as shown by Albrecht et al. [3]. In Fig. 6 the frequency dependence of the maximum value of the dynamic specific heat is reported. As similar behavior is observed with respect to that reported by Albrecht et al. for poly(ethyleneoxide) [3]. The peak values of the dynamic heat capacity extend over a large frequency range. This has been interpreted as due to the contribution to surface melting and crystallization of a group of processes, each of which with its own relaxation time.

For the TMDSC experiment on native PTFE (Fig. 5) the frequency invariance of the signal amplitude shows that the times needed by the system to reach local equilibrium at the surface of PTFE crystallites, are out of the range probed by the used method.

Lastly, we wish to remind that in the literature TMDSC studies, in the scanning and quasi-isothermal modes, have been published about other high molar mass species, in particular ultra high molecular weight poly(ethylene) (UHMWPE) [35]. In particular, two slow relaxation processes are evidenced, one of which has been related to chain diffusion. In our opinion, native PTFE and UHMWPE, similar as far as molecular weight is concerned, are morphologically different. In fact, UHMWPE, when nascent, is composed of conglomerates of poorly ordered crystals, which are susceptible of crystal growth and perfection well below the melting point. In contrast, native PTFE presents an unusually high degree of crystallinity and a much higher melting point with respect to the melt crystallized polymer. This behavior has been related to the crystalline morphology, the so-called folded ribbons [12], that cannot be more reached once the polymer has been taken to the melt state. Finally, we wish to remind that PTFE shows an unusually high melting point, which has been attributed to its low entropy of fusion with respect to other

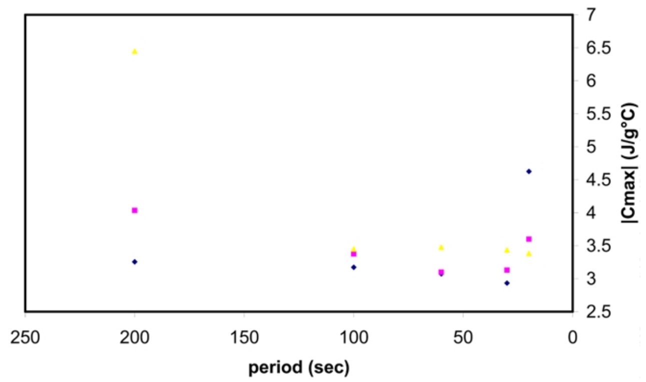

Fig. 6. Maximum value of the reversing heat capacity of PTFE for various periods of the temperature modulation. (◆): cooling experiment, (■): heating experiment (native sample), (▲): heating experiment (melt-crystallized sample).

comparable macromolecules [26]. This low value is due, in turn, to the features of the phase stable above 30 °C.

4. Conclusions

In this paper we have applied the modulated temperature calorimetry in the quasi-isothermal mode to investigate melting and crystallization of poly(tetrafluoroethylene). We have found a large reversing heat capacity in the melting and crystallization range, which can be related to the very high sliding diffusion of PTFE chains within the crystal. Moreover, the strong differences, observed in the past for the melting behavior of melt-crystallized and as-polymerized PTFE are confirmed and further evidenced. In particular, the double melting pattern, suggested for as-polymerized PTFE is well resolved and its frequency dependence examined. The characteristic times of surface melting and crystallization of the melt-crystallized sample can be estimated close to 30 s at 325 °C and 100 s at 314 °C, respectively. The peculiar trend of the thermal events in PTFE have been related to the very high sliding ability of its chains in the crystal, which in turn is due to the transition from the hexagonal to the pseudohexagonal phase, that can be assimilated to a partial (longitudinal) fusion.

References

[1] (a) Wunderlich B. Macromolecular physics. Crystal structure, morphology, defects, vol. 1. New York: Academic Press; 1973. (b) Wunderlich B. Macromolecular physics. Crystal nucleation, growth, annealing, vol. 2. New York: Academic Press; 1976. (c) Wunderlich B. Macromolecular physics. Crystal melting, vol. 3. New York: Academic Press; 1980.
[2] Hu W, Albrecht T, Strobl G. Macromolecules 1999;32:7548.
[3] Albrecht T, Armbruster S, Keller S, Strobl G. Macromolecules 2001;34:8456.
[4] Androsch R, Wunderlich B. Macromolecules 2000;33:9076.
[5] Goderis B, Reynaers H, Scherrenberg R, Mathot VBF, Koch HJ. Macromolecules 2001;34:1779.
[6] Toda A, Tomita C, Hikosaka M, Saruyama Y. Polymer 1998;39:1439.
[7] Wurm A, Merzlyakov M, Schick C. J Therm Anal 1999;56:1155.
[8] Schick C, Merzlyakov M, Minakov A, Wurm A. J Therm Anal 2000;59:279.
[9] Wurm A, Merzlyakov M, Schick C. J Therm Anal 2000;60:807.
[10] Schmidtke J, Strobl G, Thurn-Albrecht T. Macromolecules 1997;30:5804.
[11] Starkweather Jr. HW. J Polym Sci, Polym Phys Ed 1985;23:1177.
[12] Rahl FJ, Evanco MA, Fredericks RJ, Reimschussel AC. J Polym Sci Part A-2 1972;10:1137.
[13] Bassett DC, Davitt R. Polymer 1974;15:721.
[14] Suwa T, Seguchi T, Takehisa M, Machi S. J Polym Sci, Polym Phys 1975;13:2183.
[15] Nishioka A, Watanabe M. J Polym Sci 1957;24:298.
[16] Bunn CW, Howells ER. Nature (London) 1954;174:549.
[17] Starkweather Jr. HW. J Polym Sci 1979;17:73.
[18] Advanced Thermal Analysis System (ATHAS), Wunderlich B. Pure Appl Chem 1995;67:1919. http://www.utk.edu/^athas.
[19] Schawe JEK, Hohne GWH. Thermochim Acta 1996;287:213.
[20] Reading M. Trends Polym Sci 1993;8:24.
[21] Hohne GWH, Schawe JEK. Thermochim Acta 1993;229:27.
[22] Villani V, Pucciariello R, Ajroldi G. J Polym Sci, Polym Phys 1991;29:125.
[23] Villani V, Pucciariello R. J Thermal Anal 1991;37:1759.
[24] Villani V, Pucciariello R. Thermochim Acta 1992;199:247.
[25] Villani V, Pucciariello R. Colloid Polym Sci 1992;270:302.
[26] Lau SF, Suzuki H, Wunderlich B. J Polym Sci Part B, Polym Phys 1984;22:379.
[27] Pucciariello R, Villani V, Mancusi C. J Appl Polym Sci 1999;74:1607.
[28] Sperati CA, Starkweather HW. Adv Polym Sci 1961;2:465.
[29] Clark ES. Bull Am Phys Soc 1962;18:317.
[30] Weeks JJ, Sanchez IC, Eby RK, Poser CJ. Polymer 1981;21:325.
[31] Pucciariello R, Villani V. J Fluorine Chem 2004;125:293.
[32] Chen W, Toda A, Moon I, Wunderlich B. J Polym Sci Part B, Polym Phys 1999;37:1539.
[33] de Gennes PG. Scaling concepts in polymer physics, 4th ed. Ithaca: Cornell University Press; 1993. p. 1979.
[34] Schawe JEK. Thermochim Acta 1997;304:111.
[35] Hohne GWH, Kurelec L. Thermochim Acta 2001;377:141.