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Phase structure and sorption/de-sorption in poly(trimethylene terephthalate) (PTT)

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Abstract

The effect of phase structure on the sorption and de-sorption of methylene chloride in poly(trimethylene terephthalate) was studied using low and high-crystallinity pellets (22 and 54%, respectively) as the starting material. Pellets were subjected to sorption for 12 days followed by de-sorption up to 7 months. During this cycle samples were removed periodically, weighed on a microbalance to assess sorption kinetics and analyzed by thermal analysis, thermogravimetry and differential scanning calorimetry, to characterize phase structure. Sorption into low-crystallinity pellets appeared linear with respect to the square root of time and exhibited an overshoot above the final equilibrium value. Sorption into the high-crystallinity pellets suggested an induction time on the order of 1–2 h. Thermal analysis showed complex changes taking place, especially in low-crystallinity samples. Up to four phases were identified with increasing stability: amorphous, rigid amorphous, solvent-induced crystal and crystal formed from the melt.

Keywords: Poly(trimethylene terephthalate) (PTT); Methylene chloride; Sorption; De-sorption; Rigid amorphous; Solvent-induced crystals

1. Introduction

Production of polyesters, such as poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), and recently poly(trimethylene terephthalate) (PTT) often involves ‘solid stating’, the annealing at a temperature close to the melting point. Initially, even though the material is of low molecular weight, it is already solid and in the form of pellets. Solid stating allows controlled increase of molecular weight. The process may also involve significant changes in the phase structure and morphology of the pellet due to cold crystallization. Because properties of pellets affect the properties of the bulk material, it is important to understand the processes leading to formation of structure in single pellets.

This study was aimed at understanding the overall phase structure of the pellet with emphasis on the amorphous phase on the macro-scale (the scale of the whole pellet). The experimental techniques included sorption/de-sorption measurements and thermal analysis, differential scanning calorimetry (DSC) and thermogravimetry (TGA).

2. Experimental

PTT samples were provided by Shell Chemical Co. Two sets of pellets with varying initial degree of

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crystallinity were examined and designated as follows:

(a) LC: low-crystallinity.
(b) HC: high-crystallinity.

DSC analysis of the as-received samples indicated their semicrystalline nature. The initial crystallinity of the LC and HC sets was 22 and 54%, respectively. The LC samples showed cold crystallization exotherms around 63 °C with heats of transition corresponding to about 20% crystallinity. The equilibrium heat of fusion, ΔH_f° was taken as 146 J/g [1].

Sorption of a high-swelling liquid, methylene chloride ($MeCl_2$), was used to probe the morphology of the pellets. Samples (0.4–1.2 g) from each set were immersed in methylene chloride, and the tubes were held at 35 °C. Periodically, the samples were removed from the liquid, blotted dry, weighed, and returned to the liquid. De-sorption was characterized by placing the saturated pellets in open containers inside a vacuum oven held at 35 °C. Periodically, the containers were removed, weighed, and returned to the oven. Two rounds of sorption/de-sorption measurements were run, each involving four sets of pellets. On two occasions in the first round, two pellets were removed from each container and sent for thermal analysis.

Thermal analysis was performed on three sets of samples:

- Set A: samples subjected to sorption for 12 days followed by de-sorption for 15 days.
- Set B: samples from the same experiment subjected to an additional 7 months of de-sorption.
- Set C: newly prepared HC and LC samples subjected to 12 days of sorption only (no de-sorption was applied).

The as-received pellets were used for reference. DSC and TGA measurements were performed at 10 K/min heating rate under nitrogen. Sample weights varied between 10 and 25 mg.

3. Experimental results

3.1. Sorption and de-sorption

Fig. 1 shows weight gain as a function of time for the LC and HC samples during sorption and illustrates significant differences in sorption kinetics and equilibrium between the samples. The sample with 22% initial crystallinity (LC) sorbs approximately twice as much $MeCl_2$ as the sample with 54% initial crystallinity (HC). Moreover, sorption occurs much faster in the LC samples than in the HC samples. The LC sample exhibits a very clear 'overshoot' above the final equilibrium value. The HC sample does not appear to have an overshoot, but there are insufficient data points at intermediate times to state this conclusively.

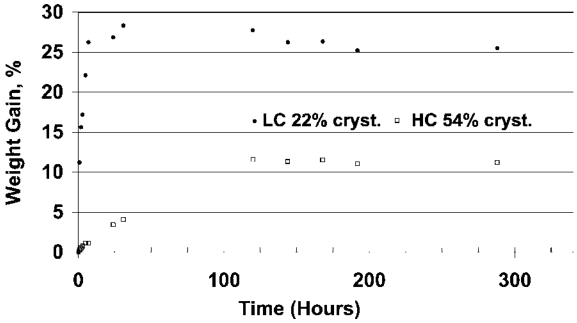

Fig. 1. Sorption of $MeCl_2$ into PTT pellets from liquid at 35 °C.

Table 1 shows the weight fraction of $MeCl_2$ in the pellets at 'equilibrium'. The final value in the sorption experiment was taken as the equilibrium sorption level. Assuming the $MeCl_2$ is soluble only in the non-crystalline regions, the weight fraction in the amorphous phase is also given. This was calculated as:

$$W\text{ (in amorphous phase)} = \frac{W\text{ (overall)}}{(1 - x_c)}$$

where x_c is the crystalline fraction.

There is a clear distinction in the weight fraction of $MeCl_2$ in the amorphous phase between low and high-crystallinity samples. The LC sample shows *significantly higher concentration* of $MeCl_2$ in the amorphous phase than does the HC sample. This trend is even more pronounced using the final values of crystallinity.

Table 1
Weight fraction $MeCl_2$ sorbed at equilibrium

Sample	Overall	Amorphous phase	
		Using initial x_c	Using final x_c
LC	0.203	0.260	0.344
HC	0.101	0.220	0.198

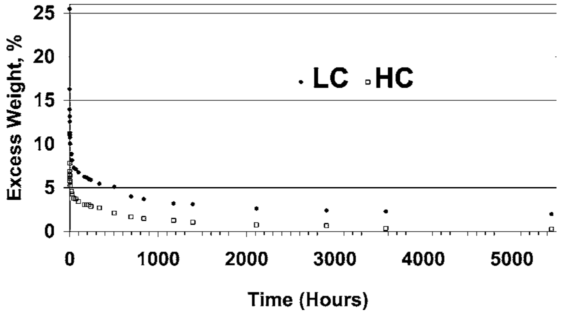

Fig. 2. De-sorption under vacuum at 35 °C of PTT pellets previously exposed to $MeCl_2$.

Following the sorption measurements, the pellets were de-sorbed up to 5500 h. The de-sorption results are plotted in Fig. 2 as excess weight (relative to initial dry weight) as a function of time. We make the following observations:

(a) After over 7 months of de-sorption, about 2% residual $MeCl_2$ remains in the LC sample.
(b) Initially, de-sorption appears faster than sorption, but de-sorption slows dramatically when the residual $MeCl_2$ reaches somewhat below 5%.

A traditional way to analyze sorption kinetics is to plot fractional uptake as a function of the square root of time. Fig. 3 shows the initial portion of the sorption data plotted on this basis. The final sorption value is used to define the fractional values, and this introduces some uncertainty into the analysis. Sorption into the LC pellets appears linear with respect to $t^{1/2}$ up to very high fractional uptake. This is consistent with a Fickian diffusion process. However, the data suggest that sorption into the HC pellets may have an 'induction time' on the order of 1–2 h. Similar behavior has been reported for the sorption of DMF into semicrystalline PET [2].

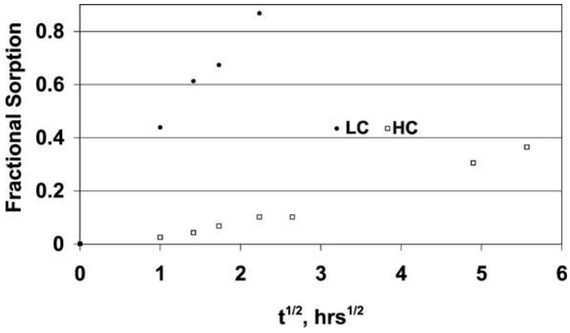

Fig. 3. Fractional sorption of $MeCl_2$ into PTT pellets at 35 °C.

Fig. 4 shows the initial portion of the de-sorption data plotted as fractional loss as a function of the square root of time. In contrast to the sorption results, the de-sorption curves for the LC and HC pellets appear similar, with the kinetics for the HC pellets only slightly slower than those for the LC pellets. The shape of these curves indicates that de-sorption kinetics decrease significantly with time.

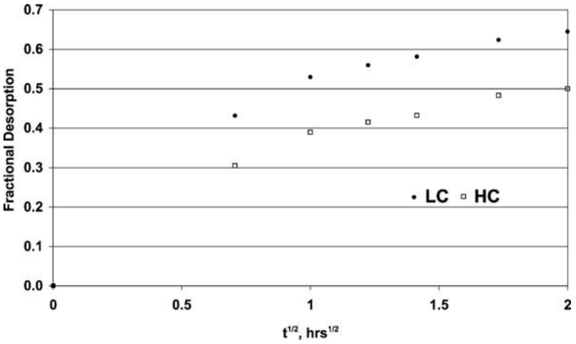

Fig. 4. Fractional de-sorption of $MeCl_2$ from PTT pellets.

3.2. De-sorption of residual $MeCl_2$ by TGA

After the sorption/de-sorption experiment was completed, samples were tested with TGA for the content of residual $MeCl_2$. The TGA method measures sample weight as a function of temperature during heating at constant rate, as shown in Fig. 5. Examination of control samples (not exposed to $MeCl_2$) showed no weight change up to 350 °C, therefore, the assumption can be made by the weight loss recorded by TGA is due to the release of residual $MeCl_2$.

The TGA curves show that the release of $MeCl_2$ takes place from room temperature (RT) to approximately 230 °C. There are, however, two distinct patterns of release recorded. The LC samples show a three-step process, with transition temperatures around 125–130 and 210 °C, while the HC samples show only two steps. In the latter case, the 210 °C transition is missing.

In step I, i.e., between RT to 125 °C, samples lost less than 1% weight. The largest mass loss of 3.5–4% was recorded in step II (125–210 °C). The LC samples

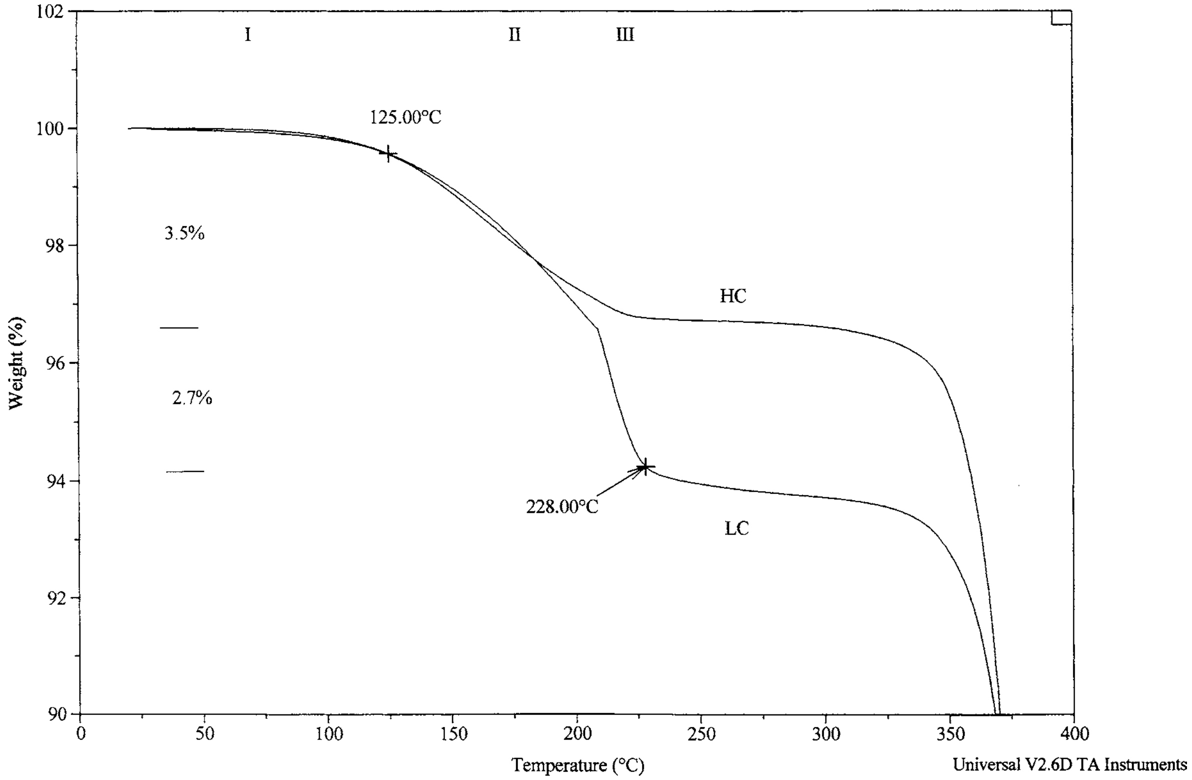

Fig. 5. TGA curves for PTT samples from set A.

show step III, where about 2.5% weight loss was recorded. The total weight loss for the LC samples was about 6%, about two times larger than for the HC samples. It was also noted that the rate of release of $MeCl_2$ increased by an order of magnitude upon each transition to a higher temperature step. Table 2 shows the rate values measured in %/min for each step.

Table 2
Rate of de-sorption at selected temperatures measured by TGA

	Rate 75 °C (%/min)	Rate 100 °C (%/min)	T_{mid} (°C)	Rate 150 °C (%/min)	Rate 175 °C (%/min)	T''_{tr} (°C)	Rate 215 °C (%/min)
Set A							
LC	0.02	0.07	128	0.29	0.41	209	1.6
HC	0.03	0.06	125	0.33	0.34	NO[a]	0.21
Set B							
LC		0.02	152		0.16		
HC		0.02	153		0.08		
Set C							
LC			103				
HC			78				

[a] Not observed.

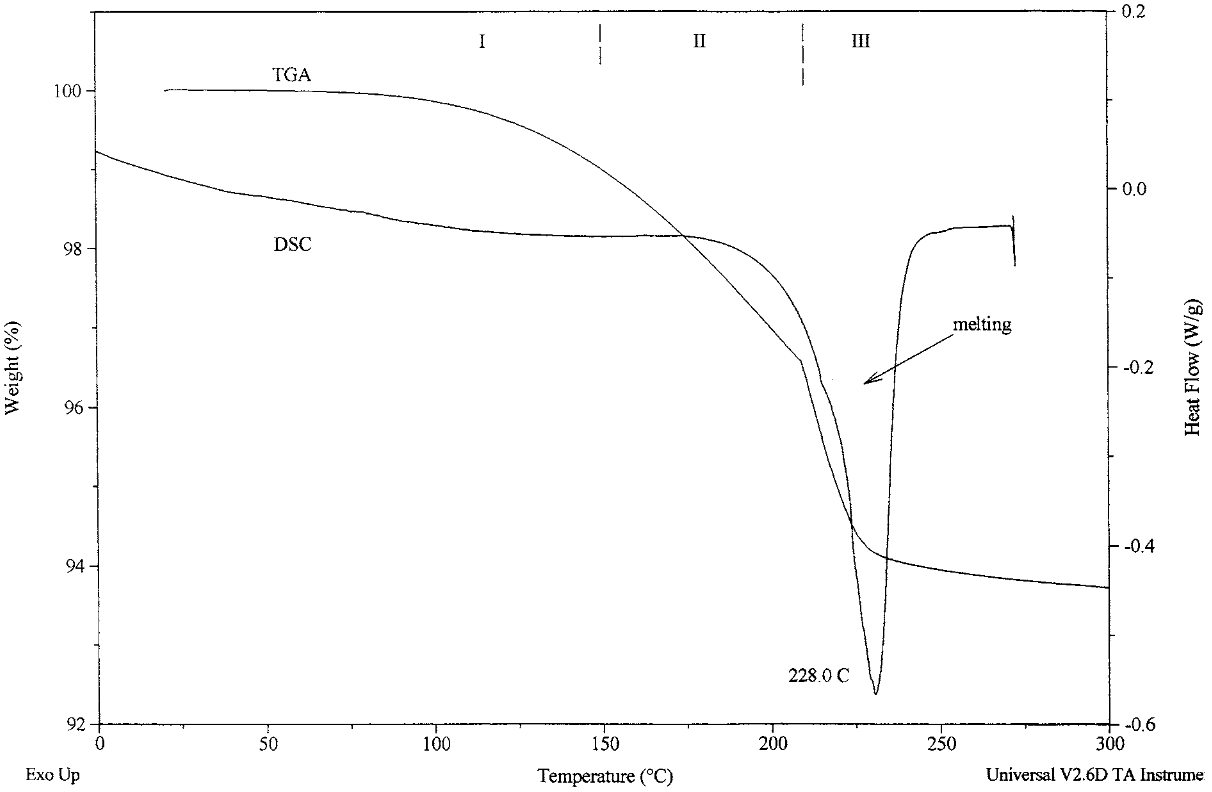

Fig. 6. TGA and DSC data for LC sample.

3.3. Thermal analysis of phase transitions by DSC

In parallel to the TGA measurements, samples from all experimental lots were analyzed for thermal transitions using DSC. In the temperature range 0–270 °C, one can identify only the melting peak as a visible feature on each curve, as shown in Fig. 6. All peak temperatures, T_{mp} are similar, but for the LC samples significant broadening of the peak is observed. The peak area was used to calculate the heat of fusion, which, in turn, allowed calculation of crystallinity. The values of T_{mp}, and crystallinity (%) are listed in Table 3 (columns 9 and 10). After exposure of the polymer to $MeCl_2$ during the sorption and de-sorption measurements, the crystallinity of the HC pellets does not change (or even decreases by a few percentage). In contrast, the crystallinity of the LC pellets increases twofold, reaching or even exceeding 40%, providing strong evidence of a *solvent-induced crystallization* (SINC) process. Further evidence for a SINC process is found in the absence of cold crystallization exotherms in the DSC curves for the LC samples.

For set B, the amount of residual $MeCl_2$ found is about two times less than that for set A. Qualitatively, both the TGA and DSC data for samples from set C are similar to those from set A. However, there are differences in the amount of released solvent. The overall content of $MeCl_2$ in set C is found to be twice as large as for samples from set A, with the majority of it residing in (and being released from) the amorphous phase. However, the amount of $MeCl_2$ present in the solvent-induced crystals in set C is similar to the amount present in corresponding samples from set A.

For set A, the trends in residual $MeCl_2$ measured by TGA and the de-sorption experiment are in qualitative agreement. For all samples in sets A and B, TGA detects more residual $MeCl_2$ than expected from the de-sorption results.

Table 3
De-sorption of residual $MeCl_2$ as measured by TGA

	Step I		Step II		Step III		Total (wt.%)	T_{mp} (°C)	Crystallinity (%)
	wt.%	Temperature (°C)	wt.%	Temperature (°C)	wt.%	Temperature (°C)			
Set A									
LC	0.5	128	3.4	209	2.7	225	6.1 (5.5)[a]	230	40
HC	0.3	125	2.9	210			3.7 (2.7)[a]	230	49
Set B									
LC	0.4	152	1.6	221	0.5	235	2.5 (1.4)[a]	230	42
HC	0.3	153	1	205	0.5	227	1.8 (0.2)[a]	228	55
Set C									
LC	1.9	103	9.1	208	3.3		12.4	231	39
HC	0.06	78	8.3				8.3	230	51
LC control								231	34
HC control								229	51

[a] Percentage of $MeCl_2$ in sample based on de-sorption data.

4. Discussion

Billovits and Durning [2] have shown that the transport behavior of organic liquids in PET below the glass transition temperature is very sensitive to the degree of crystallinity and the method of crystallization, particularly for highly compatible solvents. We followed an analogous approach to characterize the structure of PTT.

For semicrystalline materials, a sorption overshoot, as shown in Fig. 1 is usually interpreted as evidence of solvent-induced crystallization (SINC). As the solvent penetrates the amorphous phase, polymer chain mobility is increased sufficiently for further crystallization. Most of the solvent is then excluded from a region as crystallization occurs, and only a limited quantity stays as impurities. This phenomenon has been well studied in, amongst others, PET [3–5]. Table 3 confirms that SINC occurred in the LC samples. Interestingly, columns 3 and 4 of Table 1, suggests that a significant amount of $MeCl_2$ was 'trapped' in the amorphous regions when the new crystalline regions were formed.

In the TGA results, all samples have nearly identical solvent release patterns in corresponding steps I and II. Because both steps occur well below melting, one can assume that they represent evaporation from the amorphous phase. Differences between low and high-crystallinity samples are, however, observed at temperatures close to melting. While in the HC samples evaporation seems to come to completion before melting, the LC samples show yet another process, step III. The measurements indicate that crystallinity of the LC samples approximately doubles during the sorption–de-sorption experiment (due to SINC). Because the temperature range of step III coincides with the melting process, it is justified to assume that solvent released in this step comes from solvent-induced crystals upon their melting. The observed broadening of the melting peak towards low temperature is an indication of the lesser perfection of solvent-induced crystals relative to the original crystals. The peak temperatures remained unchanged, indicating that the original crystals present in samples prior to the experiment were not affected by $MeCl_2$ in the time scale of the experiments with samples of sets A and C. (At longer periods of time, however, some small amount of $MeCl_2$ may still diffuse from the amorphous to the crystalline phase, as seen in the HC samples from set B.)

The nature of the transition between steps II and III can be identified using DSC as melting. Both the breakdown of crystals and vigorous molecular motion cause evaporation to proceed with the highest possible speed.

Table 1 shows that the degree of crystallinity affects the equilibrium concentration of $MeCl_2$ in the non-crystalline phase. The same phenomenon was reported for PET by Billovits and Durning [2]. They

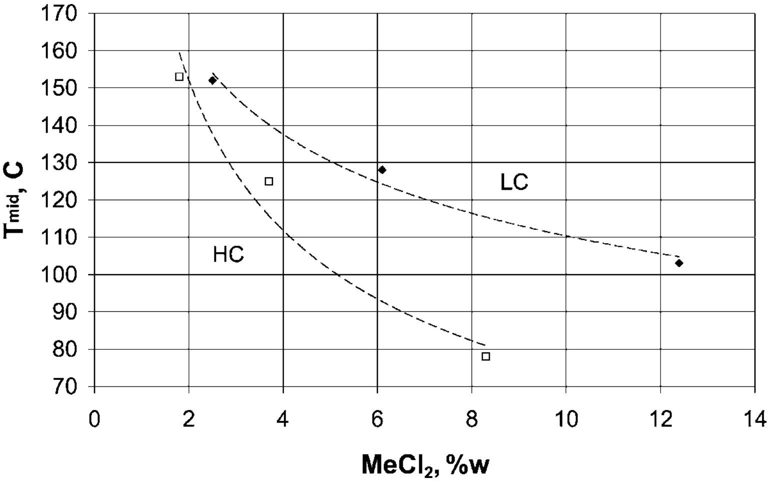

Fig. 7. The effect of $MeCl_2$ concentration on T_{mid}.

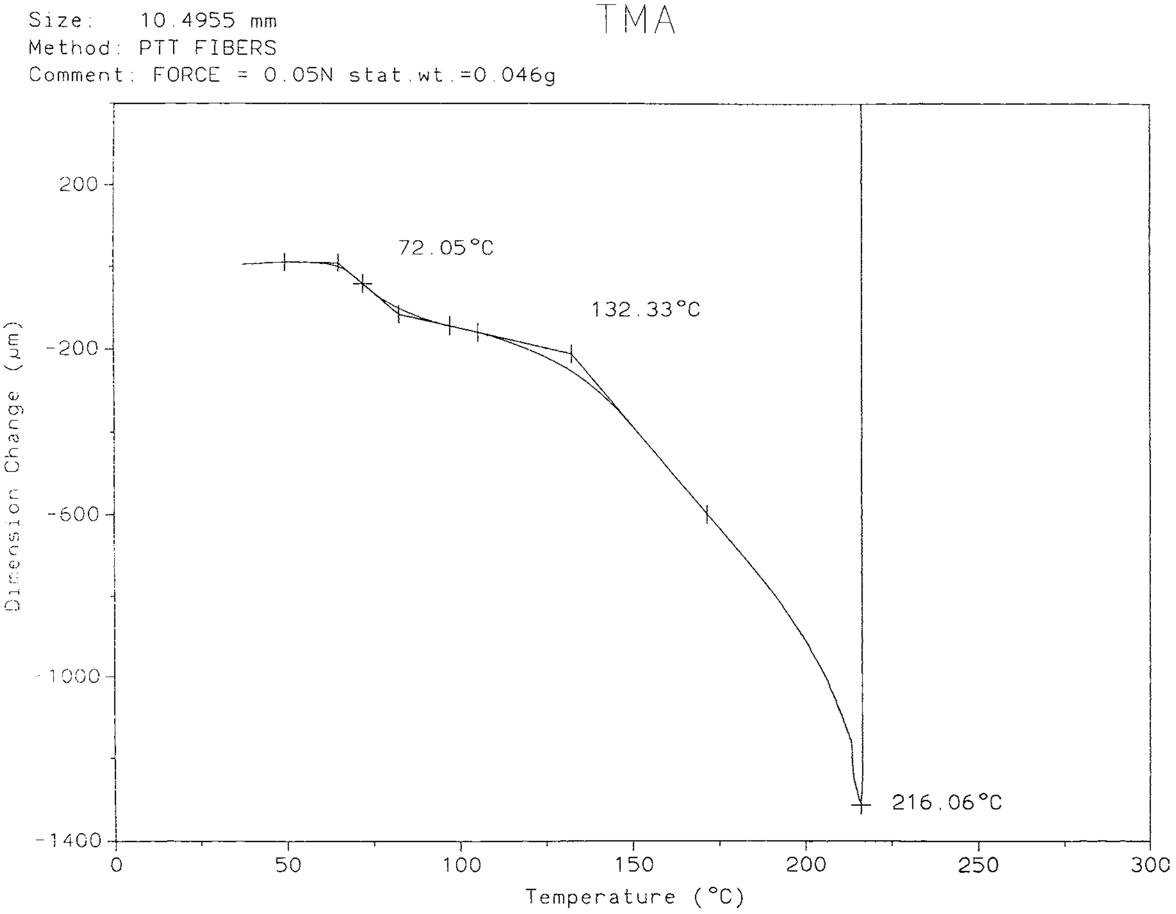

Fig. 8. Shrinkage of PTT monofilament. The curve indicates T_g at 72 °C and mid-range transition around 130 °C.

rationalized such behavior by assuming network topology for the semicrystalline polymer. Such a model allows only two phase transitions: the glass transition, at T_g, and melting, at T_m, and cannot account for a mid-range transition. Several observations are made:

(a) DSC does not show any ordering or disordering process in this temperature range close to T_{mid}, so one has to assume the amorphous phase is responsible for this transition.
(b) T_{mid} is much higher than T_g, indicating that the rigidity of the phase undergoing this transition is higher than that of the 'normal' amorphous phase; the T_g of flexible amorphous PTT was reported in the range 40–70 °C, depending on degree of crystallinity and orientation [6].

These characteristics fit the definition of *rigid amorphous phase* (RAP) [7]. A RAP in PTT was suggested previously, based on thermal analysis data [8] and especially temperature-modulated DSC data [8]. The molecular nature of T_{mid} is not clear. The increase of solvent release rate suggests an increase of molecular mobility/flexibility at T_{mid}, but the mechanism of immobilization of molecules below T_{mid} remains unknown.

T_{mid} has been recognized as a temperature of practical importance. For example, dying of PTT fibers is most effective above 130 °C. Furthermore, we have noticed that T_{mid} depends quite strongly on the content of solvent in the sample. Fig. 7 shows the dependence of T_{mid} on the initial concentration of $MeCl_2$ at RT for samples with both high and low initial crystallinity. The curves are included to indicate trends suggested by the limited data. Further work is needed to understand how T_{mid}, solvent, and crystallinity are related.

Although the nature of this transition is not clear at present, its temperature (130–150 °C observed here by TGA) is very similar to the "transition" temperature recorded earlier by thermomechanical analysis (TMA) during shrinking of PTT monofilaments, as shown in Fig. 8. At this temperature, a sharp change in shrinkage rate was observed.

5. Summary

Based on the current and previous observations, four phases can be identified in PTT: (1) random amorphous, characterized by the glass transition temperature, T_g; (2) rigid amorphous, manifesting itself by the mid-range transition temperature, T_{mid}; (3) solvent-induced crystals, which cause broadening of the melting peak towards low temperature; (4) 'normal' crystals, obtained during crystallization of the melt having characteristic melting point, T_m. The relative content of each phase depends on initial crystallinity, the presence of solvent, and most likely, orientation and pressure (not studied here). All phases can be detected by a variety of experimental methods, and their relative stability can be judged approximately by their transition temperatures as follows: $T_g < T_{mid} < T_m$ of SINCs $<T_m$.

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