Polymer Bulletin 51, 285–291 (2004)
DOI 10.1007/s00289-003-0221-5

Polymer Bulletin

Raman Spectroscopy Study of Poly(trimethylene terephthalate) Crystallization

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Received: 8 August 2003/Revised version: 3 November 2003/ Accepted: 4 November 2003

Summary

Raman spectroscopy was used to study the crystalline states of poly(trimethylene terephthalate) (PTT). There were significant spectral differences between the PTT melt and the crystallized PTT. The 909 cm^{-1} band, associated with the C-C stretching of the trimethylene glycol residue, was found to be a suitable band for quantitative measurements of PTT crystallinity. Both the 847 and 1176 cm^{-1} benzene ring breathing modes could be used as the internal reference bands, however, the use of the 1176 cm^{-1} band was more sensitive to crystallinity changes. Two other C-C glycol residue stretching bands, 1116 and 1103 cm^{-1}, were found to relate to the crystalline and amorphous phases, respectively, from annealing experiment.

Introduction

Poly(trimethylene terephthalate) is a new commercial aromatic polyester. Compared to the even-numbered polyesters such as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT), PTT, with three methylene units in its glycol moiety, shows significantly different physical and mechanical properties. Studies [1,2] showed that some of these properties were either directly or indirectly influenced by the crystallization process. As such, PTT crystallization behavior and morphology had been investigated rather extensively using wide-angle x-ray diffraction [3], optical and electron microscopies [4], differential scanning calorimetry (DSC) [5] and infrared spectroscopy [6].

Raman spectroscopy has proven to be a useful tool in studying PET structural changes during crystallization [7, 8]. Compared to PET, Raman spectroscopy study of PTT is relatively scarce. Ward and Wilder [9] were the first to analyze PTT Raman spectra and to assign a series of Raman bands to specific PTT polymer chain conformations. Their assignments were based on separating the vibrational modes of the para-disubstituted benzene ring from those of the glycol residue. Three regions of the spectrum were found to be sensitive to crystallization: regions around 800-950 cm^{-1}, 1400 cm^{-1} and 1100-1200 cm^{-1}. Using rapid-scanning Raman spectroscopy, Bulkin, *et al.* [10] studied the cold crystallization kinetics of PTT film by following changes in the 1220 cm^{-1} band intensity when the sample was isothermally annealed above its glass transition temperature. The 1220 cm^{-1} band was used because it is a new band which appeared only upon annealing, and the intensity ratio of this band to that of an internal 1174 cm^{-1} reference band was found to have a linear correlation with the polymer's density, and therefore its crystallinity. However, the origin of the band was unknown, and it was not reported in Ward and Wilding's [9] Raman band assignments.

In this study, we found the 909 cm^{-1} C-C stretching of the methylene groups to be a more suitable band for measuring PTT crystallinity because the origin of this band is well established and its intensity increases linearly with crystallinity. Theoretical calculations of the accordion-like stretching of C-C bonds in a series of poly-*n*-methylene chains showed a Raman active band at ~910 cm^{-1} when n=3 [11]. Although Ward and Wilding [9] did not include this band in their table of PTT Raman bands, they did discuss and thought it was reasonable to assign this band to vibrations of the crystalline glycol residue because of the increase in intensity with annealing. In addition, we found the 909 cm^{-1} band intensity is much stronger and more sensitive to changes in sample crystallinity than the 1220 cm^{-1} band used by Bulkin, *et al.* [10], and therefore would give a more accurate measurement of PTT crystallinity. In this note, we re-examine and discuss the bands associated with PTT's glycol residue conformation, report the relationship of the 909 cm^{-1} band to PTT crystallinity, and demonstrate a quantitative *in-situ* Raman spectroscopy method for estimating PTT crystallinity during fiber extrusion.

Experimental

Fiber formation

Clear PTT polymer with an intrinsic vsiscosity of 0.92dl/g was supplied by the Shell Chemical Company, Houston, Texas. The polymer was melt spun into fibers using a Hills, Inc., 1-inch diameter single-screw extruder with a L/D ratio of 30:1 in the Fiber & Polymer Science research facilities of the School of Materials Science & Engineering at Clemson University. A four-zone extruder with a flat temperature profile of 257°C for each zone was used for spinning. A three-hole spinneret with a hole diameter of 1 mm and a L/D ratio of 4 was used to obtain the fibers. The as-spun fibers were taken up on a bobbin at a slow speed of 250m/min. using a Barmag SW4 winder. Such low take-up speed was insufficient to induce orientation to the fibers.

Differential scanning calorimetry (DSC)

PTT crystallinity was measured using a TA Instrument DSC 2920 calorimeter in a nitrogen atmosphere. The instrument was calibrated with an indium standard. Samples with a mass of approximately 3-5 mg were heated from 0°C to 300°C at a heating rate of 10°C/min., and then cooled to 0°C at the same rate. The degree of crystallinity was calculated by dividing the experimentally determined heat of fusion, after subtracting the cold crystallization exotherm, by the heat of fusion of a 100% crystallized PTT, which is 30 kJ/mol [12].

Raman spectroscopy

A Renishaw system 100 Raman spectrometer coupled with a remote Renishaw fiber optic probe head was used to record the spectra of the PTT fibers. A high power 500 mW NIR diode laser (785 nm) was employed. The probe head was equipped with an Olympus 20X ultra-long working distance (1.2 cm) objective. When focused on the fiber a depolarized laser light of 39 mW was delivered to the sample. Depolarized laser radiation was used to measure the fiber crystallinity since an orientation independent information is required in this kind of study [13].

Results and Discussion

Raman Bands Associated with PTT Crystalline Phase

Wide-angle x-ray diffraction (WAXD) and electron diffraction (ED) studies showed that PTT crystal structure is triclinic [14]. The glycol residue in the crystal consists of only the gauche conformation and the trans conformation is associated with the amorphous phase [9, 14]. The description of the bands in this work was based upon the comparison of Raman spectrum of both the amorphous and the semi-crystalline samples. Peaks related to the glycol residue and intensified upon annealing are assigned to the gauche conformation in the crystalline phase.

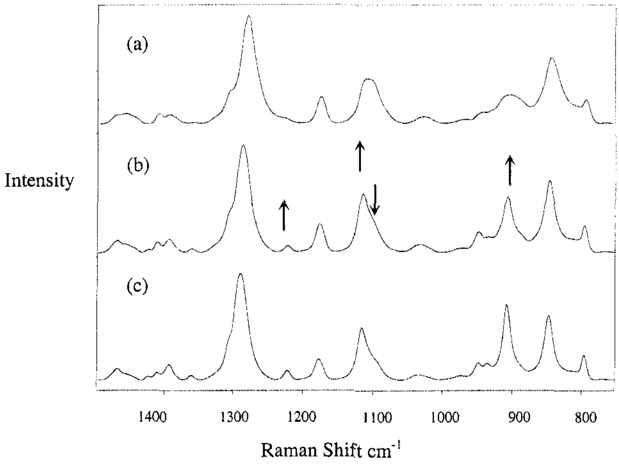

Figure 1: Raman finger print regions of PTT (a) obtained at 46 cm below the spinneret, (b) with low crystallinity and (c) with high crystallinity. (Arrows indicate peak intensity increased or decreased with annealing)

Figure 1 (a) to (c) shows the Raman spectrum of PTT melt, and PTT fibers with low and high crystallinities, respectively. Spectrum (a) was collected in real time with the Renishaw probe placed at 46 cm below the spinneret while the fiber was being spun;

spectrum (b) was collected on the as spun, undrawn fiber after annealing at 50°C for two hours, and spectra (c) was collected on the as spun, undrawn fiber after annealing at 90°C for two hours. The finger print region (750-1500 cm^{-1}) of the three spectra showed large spectral differences as a consequence of the different crystallization conditions. The key peaks in this discussion are indicated by arrows either pointing upwards or downwards indicating the intensity increases or decreases, respectively, upon annealing. The spectral changes are in broad agreement with those reported by Ward and Wilding [9] and by Bulkin, *et al.* [10], with some new observations.

Fairly large differences resulting from crystallization occurred in the region between 800 cm^{-1} and 950 cm^{-1} [8]. We paid particular interest to the 909 cm^{-1} band which significantly intensified as PTT solidified and crystallized. From the theoretical calculations of the accordion-like C-C stretching of poly-*n*-methylene chains [11], the 909 cm^{-1} band can be definitively assigned to the stretching of the three methylene groups of the glycol residue. Since the band intensity increases with crystallinity upon annealing, we assign this band to the crystalline phase gauche methylene conformation, and confirm Ward and Wilding's earlier thoughts.

The second band, which is also associated with the accordion-like C-C stretching, occurs around 1100 cm^{-1} [11]. An obvious change in the peak shape was observed with the appearance of a shoulder when PTT melt was solidified and annealed from low to high crystallinities. The peak could be resolved into two components using a curve fitting program resulting in one peak centered at 1116 cm^{-1} and the other at 1103 cm^{-1} (Figure 2). The intensity of the 1116 cm^{-1} peak was found to increase and its shape sharpened while the intensity of the 1103 cm^{-1} peak decreased and became broader as PTT crystallized (Figure 1). Therefore, we assign the 1116 cm^{-1} band to the crystalline phase gauche conformers, and the 1103 cm^{-1} band to the trans conformers.

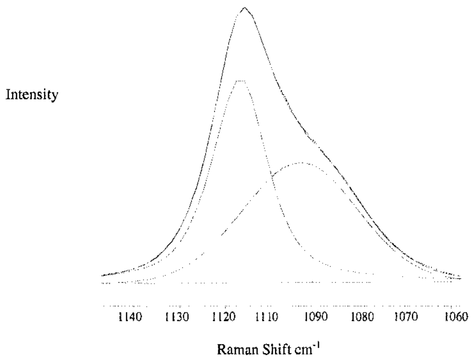

Figure 2: Deconvoluted 1116 and 1103 cm^{-1} C-C glycol residue stretching bands.

The 950 cm^{-1} band, which is tentatively assigned to the gauche conformation of the glycol residue in the amorphous phase exists in both the amorphous and the highly crystalline phases. A new band centered at 937 cm^{-1} was generated and intensified upon annealing. We know that annealing results in an increase in the crystallinity by the rearrangement of polymer chains, hence it is reasonable to tentatively assign the 937 cm^{-1} band to the vibration of the crystalline glycol residue.

Quantitative measurement of PTT crystallinity

From the above discussion, among the various bands which intensify upon annealing, the 909 cm^{-1} band is the most suitable one for crystallinity measurement. In order to establish a quantitative relationship between Raman scattering and the crystallinity, fibers of differing crystallinity were prepared by annealing under a constant load of 15 g from 50 to 90°C at 10°C increment for 120 min. Their crystallinities were measured by DSC.

The spectral region from 750 to 1500 cm^{-1} was analyzed for both the low and high crystallinity PTT fibers by using the spectral decomposition procedure previously described [13]. A typical curve-fitting result is shown in Figure 3. The peak height obtained from curve fitting was used to estimate the intensity of the Raman scattering. The benzene ring C-C breathing mode 847 cm^{-1} band was used as an internal standard since its intensity did not change with sample crystallinity and draw ratio [15]. Alternatively, the 1176 cm^{-1} used by Bulkin, *et al.* [10] could also serve as the internal reference.

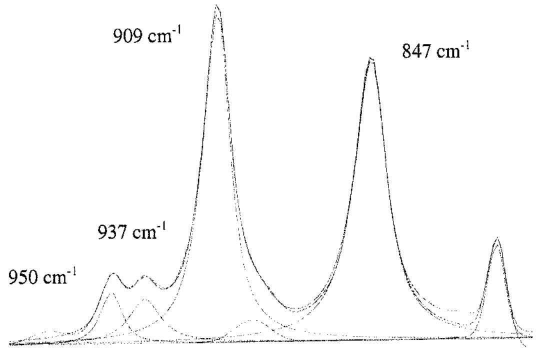

Figure 3: The deconvoluted 847, 909, 930 and 950 cm^{-1} bands of the undrawn PTT fiber after annealing at 90 °C for 2 hours.

Figure 4 shows the plots of the 909/847 cm^{-1} and 909/1176 cm^{-1} intensity ratios against the crystallinity determined from DSC for the undrawn sample. Both plots showed good linear relationships. The 909/1176 cm^{-1} intensity ratio is, however, more sensitive to crystallinity changes than is the 909/847 cm^{-1} intensity ratio. Therefore, the 1176 cm^{-1} band is a better internal reference than is the 847 cm^{-1} band.

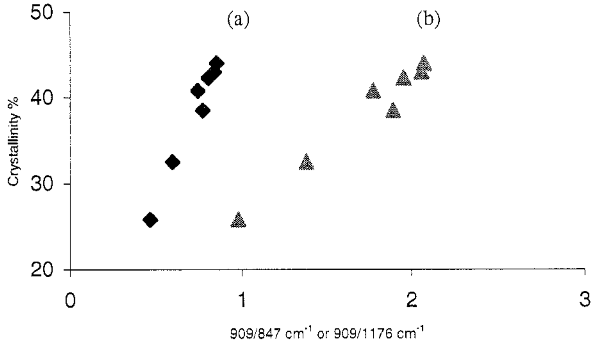

Figure 4: Linear correlations of the (a) 909/847 cm^{-1} and (b) 909/1176 cm^{-1} band intensity ratios with sample crystallinities measured from a DSC.

The use of the 909 cm^{-1} band has several advantages over the 1220 cm^{-1} for studying the crystallization of PTT. First, it is more intense than the 1220 cm^{-1} band and is consequently more accurate in estimating the crystallinity. Second, the band assignment is unambiguous whereas the origin of the 1220 cm^{-1} band is unknown except that its intensity increases upon annealing.

Conclusion

Raman spectroscopy has shown to be a useful method for studying the crystallization of PTT polymer. The 909 cm^{-1} band was assigned to the gauche methylene conformers of the crystalline region, and the 1116 and 1103 cm^{-1} bands were assigned to the crystalline and amorphous phases, respectively. The intensity ratios of the 909/847 cm^{-1} and 909/1176 cm^{-1} bands were found to correlate linearly with PTT's crystallinity obtained from a DSC. The 1176 cm^{-1} band was found to be a better internal reference than the 847 cm^{-1} band for crystallinity measurement because the 909/1176 cm^{-1} intensity ratio is more sensitive to crystallinity changes. In this work we established that the Raman probe has the advantage of carrying out *in-situ* measurements of unoriented as-spun fibers. In future work we will be exploring *in-situ* crystallization and deformation studies of PTT using the bands discussed in this note.

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