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Ti is commonly used as a catalyst for the polymerization of poly (butylene terephthalate) (PBT) commercially. The segregation and distribution of these Ti catalyst residuals in the solid state morphology is perplexing and deserves serious attention. Recently, we have attempted to address this question by performing real-time SAXS experiments on PBT samples with either 50 or 500ppm Ti under isothermal crystallization conditions at 2050C and 2100C.

Figure 1 shows the variation of SAXS invariant Q as a function of crystallization time for four measurements. It is known that for semicrystalline polymers, Q can be related to a structure parameter by the following equation:

$$Q = V_s X_c (\Delta\rho)^2$$

where  $V_s$  is the volume fraction of crystallized structures,  $X_c$  is the linear crystallinity, and  $\Delta\rho$  is the averaged electron density difference between the crystalline and amorphous phases. Linear crystallinity can be easily calculated from the ratio of crystalline layer to amorphous layer thickness, and the volume fraction  $V_s$  can be derived from bulk crystallinity determinations from WAXD data. Given these values ( $V_s$  and  $X_c$ ), the observed SAXS invariant Q is proportional to  $\Delta\rho^2$ . From Figure 1, one observes that the rate of crystallization increased at the lower isothermal crystallization temperature (greater undercooling) as expected. Furthermore, this figure clearly displayed that Q's for samples with 500 ppm Ti are consistently smaller than those for samples with 50 ppm Ti.

From SAXS data, we found that all these samples have the same degree of linear crystallinity, even though the long periods are slightly larger for samples with a smaller degree of undercooling. From WAXD data measured simultaneously with SAXS data, we found that there is no change of mass crystallinity between 50 ppm and 500 ppm samples. In addition, from DSC data, both samples have the same bulk crystallinity at equivalent crystallization temperatures. Therefore, the difference in Q has to be ascribed to  $\Delta\rho$ . We speculate that the Ti catalyst remains in the amorphous phase between crystalline lamellae and increases the amorphous phase density by forming Ti centered aggregates. As a result,  $\Delta\rho$  becomes smaller and thus so is the scattering invariant Q. More work is necessary to quantitatively understand segregation and distribution of these Ti catalyst residues.

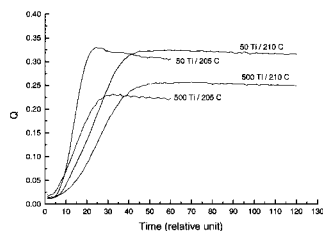


Figure 1. SAXS invariant vs. time.