

Reduction in Surface Energy of Nanocrystals by Highly Conjugated Organics

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Introduction

It is known that the addition of organic pigments to polypropylene can modify crystallization of the polymer [1, 2]. This behavior is known for a wide range of organic pigments that are nanostructured, aggregated, crystalline materials. We were the first to report on the structure of these organic pigment aggregates in work done on the UNI-CAT ultrasmall-angle x-ray scattering (USAXS) instrument at APS [3]. In conjunction with studies of pigment aggregation, we serendipitously observed an interesting effect of these pigments on the polymer lamellar crystalline thickness as a result of the presence of the nanostructured organic pigments, which is the subject of this report.

Polymers crystallize into lamellar crystals with an aspect ratio similar to that of a sheet of paper and a thickness typically on the order of 10 nm. The lamellar crystalline form is due to differences in the surface energy for the crystalline faces, particularly the high surface energy of the chain fold surface, as described by the Hoffman-Lauritzen form of the Gibbs-Thompson (Kelvin) equation:

$$t = \frac{2\sigma_{fold}T_{\infty}}{\Delta H_f(T_{\infty} - T_c)},$$

where t = the lamellar thickness, σ = the surface energy of the chain fold surface, and T_{∞} = the melting temperature of an infinitely thick crystal. Any reduction in the chain fold surface energy should lead to a close-to-proportional reduction in the lamellar thickness. Reduction in the fold surface energy can also lead to stabilization of normally unstable crystalline forms. Polypropylene can grow in two common crystal forms, the ordinarily seen α monoclinic form and a rarer hexagonal β form that can be observed in strained samples, for instance. The β crystals form under a variety of conditions, one of which is the presence of quinacridone pigments. The fraction of β crystals formed in the presence of organic pigments is typically on the order of 10%, with the remainder of the crystals being of the more typical α form. The modification of polypropylene crystal structure by organic pigments is rather intriguing since we have observed both traces of β

crystal and a dramatic shift in the mean lamellar thickness in the presence of an extremely wide range of crystalline organic pigments, the only common feature among which is the presence of highly conjugated chemical structures. Figure 1 shows USAXS data from neat polypropylene and polypropylene with 5-wt% quinacridone Red 122 from Sun Chemical Corporation isothermally crystallized at 140°C and quenched to room temperature. The SAXS data are presented in a log-log plot to highlight power-law regimes that go from large sizes (close to 1 μm) on the left to small sizes (on the order of 10 \AA) on the right. The top curve is for the red pigment sample and the first power-law, with a slope of about -1.6 reflecting the negative of the mass-fractal dimension of the pigment aggregates. The knee at about 0.003 \AA^{-1} reflects a Guinier regime for the smooth-surfaced faceted pigment crystals that make up the aggregates ($R_g \cdot 20$ nm). Following this knee is the surface scattering from the smooth-surfaced pigment particles and a hump associated with stacks of the polymer lamellae. The stacking period together with the degree of crystallinity (65% in both cases) indicate lamellae on the order of 6 nm in thickness, while the neat polypropylene shows a lamellar thickness of about 12 nm. The shift in lamellar thickness results entirely from the pigment's presence and reflects a reduction in the surface energy of the lamellar crystals by a factor of about two.

Surface nucleation of the polypropylene due to the pigments seems improbable since (1) the pigment particles are much smaller than the lateral dimension of the polymer lamellae (on the order of 1 μm); (2) most of the pigment surfaces are very smooth (a few are composed of nanoclusters with rough surfaces), as seen in transmission electron microscopy (TEM) micrographs and supported by USAXS data from UNI-CAT; and (3) an identical value for the lamellar thickness is seen for an extremely wide range of pigments with very different crystalline forms, lattice spacings (differing by an order of magnitude), and chemical species, except that all of the pigments have a high degree of conjugation that is associated with their color.

It is interesting to note that stabilization of nanocrystals by conjugated organics is known in the inorganic synthesis of monodisperse crystalline nanoparticles of several silver halides used in the photographic industry as

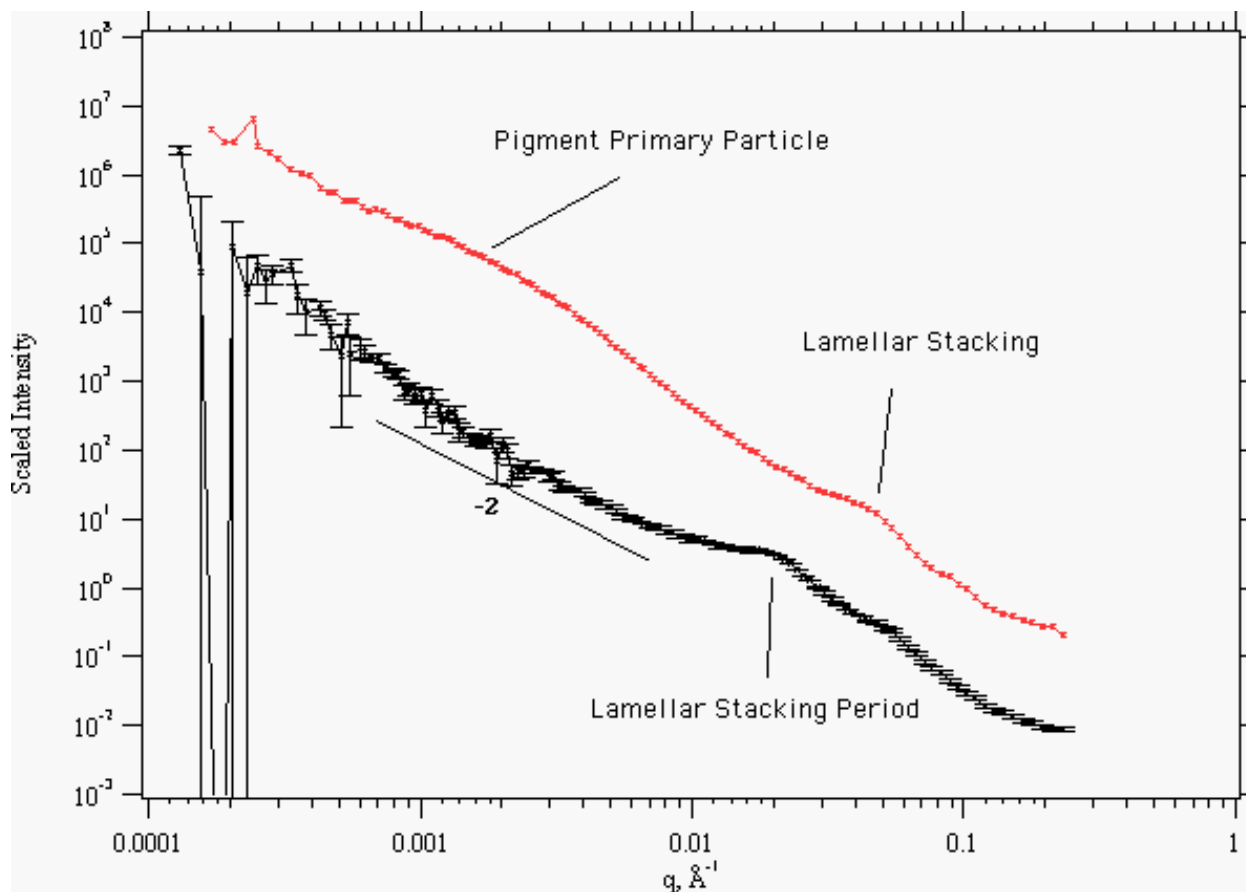


FIG. 1. USAXS data from neat polypropylene and polypropylene with 5 wt% quinacridone Red 122 isothermally crystallized at 140°C and quenched to room temperature.

discussed by Matijevic, Sagimoto, and others [4, 5]. In this case, azide compounds chemically similar to the quinacridone pigments are routinely added to synthesis of inorganic nanocrystallites to prevent recrystallization to larger, more stable species, while the mechanism is unknown. Again, the Ostwald-driven recrystallization in these inorganic systems is associated with surface-energy-controlled Gibbs-Thompson effects. We have recently made polypropylene/azide composites with identical results to the quinacridone data shown above.

Highly conjugated organics such as the azides used in silver halide nanocrystallization and pigments used in polypropylene are capable of strong van der Waals interactions because of the high mobility of pi-electrons. It is also known that these pigments are marginally soluble in polypropylene, so a sufficient amount for surface coverage of nascent crystals by van der Waals interaction in polypropylene is possible. We believe that such surface coverage and an associated reduction in the surface energy of the crystals (by a factor of about two) could account for the observed shifts in nanocrystallite

size in polypropylene as well as in aqueous growth of silver halide crystals. The effects are more dramatic in the ionic silver halide system as might be expected for van der Waals interactions. We are in the process of verifying this proposition in several other systems using by USAXS measurements at UNI-CAT.

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