

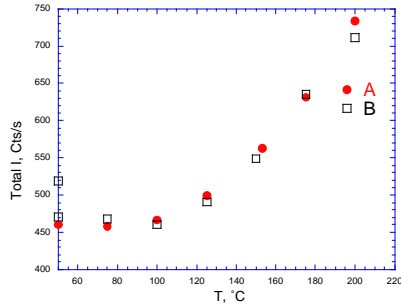
# MICROSTRUCTURE ANALYSIS USING TEMPERATURE INDUCED CONTRAST VARIATION IN SMALL-ANGLE SCATTERING

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## Introduction

The work described below seeks to exploit the fact that, under certain favorable conditions, the intensity of the small-angle scattering (SAS) from certain polymeric materials varies strongly with temperature even though no microstructural changes are taking place. These effects are quite dramatic in semicrystalline polymers near their glass temperature. Figure 1 shows an example of this effect from recently published work[1].



**Figure 1.** - Raw total detector count as a function of temperature from Ref 1.  $T_g$  for this polymer is approximately 95 °C. See Case I under “Applications” for details. “A” and “B” designate samples prepared under two different crystallization conditions.

Most, if not all, of the intensity variation in these cases arises from changes in the contrast factors that control SAS, namely the differences in scattering length density between the crystalline and amorphous elements in the microstructure. At the glass temperature there is a sharp change in the thermal expansion coefficient of the amorphous component, which leads to a discontinuity in the temperature derivative of the scattered intensity. This paper seeks to expand the number of systems in which this behavior is observed in an effort to determine qualitatively whether the temperature induced contrast variation (TICV) effect can be usefully exploited in a systematic manner.

## Theory

Temperature-induced contrast variation is a disarmingly simple effect that can be easily appreciated by considering a Taylor series expansion of the scattered intensity with respect to temperature:

$$I(\bar{Q}, T) = I(\bar{Q}, T_{ref}) + \left. \frac{d}{dT} (I(\bar{Q}, T)) \right|_{T_{ref}} (T - T_{ref}) \quad (1)$$

$I(\bar{Q}, T)$  is the intensity scattered into an element of solid angle at wavevector  $\bar{Q}$ ,  $T$  is the temperature, and  $T_{ref}$  is a suitably chosen “reference temperature.” We take explicit account of any anisotropy that may be present in the structure by treating the wavevector as a three-dimensional entity. As will be shown later, anisotropy is extremely useful for confirming the identities of microstructural features.

Since modern SAS patterns are recorded digitally it is easy to subtract them from one another. The result of subtracting two SAS patterns at different temperatures is:

$$I(\bar{Q}, T) - I(\bar{Q}, T_{ref}) = \left. \frac{d}{dT} (I(\bar{Q}, T)) \right|_{T_{ref}} (T - T_{ref}) \quad (2)$$

The strongest contributions to the right hand side are those that vary most strongly with temperature. Contributions to the full scattering pattern that are only weakly temperature dependent largely cancel out in the

subtraction. Such contributions include incoherent backgrounds, solvent scattering, and some matrix effects in two-phase systems. It is normally quite difficult to account for these effects when analyzing full patterns, so that the difference method may offer considerably enhanced resolution in a number of instances. The power of difference scattering has been demonstrated in the context of anomalous scattering[2] or with isotopic substitution in SANS[3], but we are unaware of previous studies where simple temperature effects have been used to provide a similar capability.

Setting aside for a moment the question of overall intensity units it is common to treat the scattered intensity from two-phase systems as being proportional to[4,5]:

$$I(\bar{Q}, T) = ( \Delta \rho )^2 S(\bar{Q}, T) P(\bar{Q}, T), \quad (3)$$

where  $\Delta \rho$  represents the contrast factor,  $S(\bar{Q}, T)$  represents the interference effects that arise between scattering entities, and  $P(\bar{Q}, T)$  accounts for the internal structure of the scattering entities when they are treated as discrete particles.

In the present work we stipulate that the reference temperature is outside the range of temperatures at which gross structural transformations such as melting, annealing, or changes in orientation texture take place. While it may be possible to observe manifestations of temperature dependence of the  $S$  and  $P$  factors, the contributions that arise from the temperature dependence of the contrast factor are typically much more dramatic.

## Application: Lamellar Microstructures in Semicrystalline Polymers

As a first example of the power of the temperature-induced contrast variation technique we consider the scattering from a semicrystalline polymer well below its melting point. Our efforts to understand just such a system called our attention to these matters in the first place (see Figure 1).

In this instance the dominant microstructural entities are stacks of lamellae organized into spherulites. The observed scattering contrast is attributable to the difference between the scattering length densities in the alternating amorphous and crystalline layers within these stacks. To first order in temperature we can express the contrast factor as:

$$\Delta \rho = (1 - \chi_c) \rho_c + \chi_c \rho_a \quad (4)$$

where  $\rho_c = \rho_c^0 + \alpha_c (T - T_{ref})$ ,  $\rho_a = \rho_a^0 + \alpha_a (T - T_{ref})$ ,  $\chi_c$  is the volume fraction crystallinity,  $T = T - T_{ref}$ , and  $\alpha_c$  and  $\alpha_a$  are the thermal expansion coefficients of the crystalline and amorphous phases respectively.

Substituting Eqn 4 into Eqn 2 and carrying out the differentiation yields:

$$I(\bar{Q}, T) - I(\bar{Q}, T_{ref}) = 2 \chi_c (\rho_c^0 - \rho_a^0) \left\{ \alpha_c (T - T_{ref}) + \frac{1}{2} (\alpha_c - \alpha_a) (T - T_{ref})^2 \right\} F(\bar{Q}), \quad (5)$$

where  $F(\bar{Q}) = (1 - \chi_c) \rho_c^0 + \chi_c \rho_a^0$ . We have merged the  $S(\bar{Q})$  and  $P(\bar{Q})$  functions into a single function  $F(\bar{Q})$  because the lamellar stack microstructure does not allow for the separation of these two terms. We assume that  $F(\bar{Q})$ , the “form factor,” does not depend on the temperature. Eqn 5 predicts that the amplitude of the difference pattern increases as a simple polynomial function of  $T$  without any noticeable shifts in the peaks and valleys of the pattern. The relative strengths of the linear and quadratic terms in the polynomial are controlled by the differences between the bulk densities and the thermal expansions of the crystalline and amorphous phases. As long as there is no morphological change taking place the patterns should be reversible with respect to temperature.

While temperature-induced contrast variation may not be a large effect, it can be readily observed. With proper precautions the technique yields difference scattering patterns that allow the observer to focus on specific features in the microstructure.

The most significant simplification in Eqns 3 through 5 is that the scattering is controlled by a single mechanism. It might be feasible to account for multiple scattering mechanisms by treating  $I(\bar{Q}, T)$  in Eqn 2 as a mixture of components and then exploring the temperature dependence of each component.

In the remainder of this paper we will use Eqn 5 to analyze data from experiments on several different semicrystalline polymers. Generalizations of the method to other classes of materials will be the subject of future work.

## Case I - Syndiotactic Polystyrene

Figures 1 and 2 are from previously published work[1] that piqued our interest in the TICV phenomenon. Until data from more refined experiments

becomes available the formalism described in the preceding section accounts for the features shown in the figures as follows:

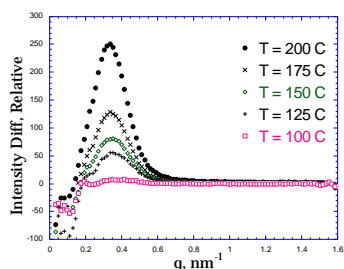
1. The sharp change in slope for the total detector count (Figure 1) in the vicinity of 100 °C arises from the glass transition in this polymer. This value is consistent with values estimated by other means[6].

1a. The amorphous and crystalline densities are essentially identical for  $T < T_g$  ( $\rho \approx 0$ ). The evidence for this is the complete absence of the characteristic peak for the long period at and below  $T_g$ .

1b. The thermal expansion coefficients of the crystalline and amorphous phases differ only slightly below  $T_g$  ( $\alpha \approx 0$ ). This accounts for the very weak temperature variation in the integrated  $I(q)$  over the range 50 °C  $< T < 100$  °C.

1c. The thermal expansion coefficient of the amorphous phase increases drastically at  $T_g$  ( $\alpha \approx 0, \alpha \gg 0$  for  $T > T_g$ ). This accounts for the strong temperature dependence for  $T > T_g$  in Figure 1.

2. The absence of shifts in the peak positions for the circularly averaged difference files (See Fig 2) obtained between  $T_g$  and 200 °C is evidence for the stability of the lamellar stack microstructure.



**Figure 2.** Difference  $I(q)$  plots from ref 1. Note that the peak positions and widths remain unchanged while the amplitude increases with increasing  $T$ .

3. The relatively small negative values found at small  $q$  in Figure 2 reflect small shifts in the amplitude of the central scattering peak. We suspect that these represent annealing of structures on distance scales larger than the lamellar stacks (e. g. spherulites or voids). Such shifts seem to be commonplace in TICV experiments, but further work is required to elucidate their origin.

4. The intensities in Figure 1 are raw count totals over the entire detector. They therefore include contributions from the unscattered primary beam as well as a “matrix scattering” scattering that is distinct from the lamellar scattering. This matrix scattering is the major contributor to the baseline intensity (the values below 100 °C) in Figure 1. The origin of this scattering remains elusive.

### Case II - poly(4-methyl pentene-1)(P4MP)

Poly(4-methyl pentene-1) is another polymer whose amorphous and crystalline densities are known to be very similar at temperatures below the glass temperature of the polymer[7]. In order to see if TICV effects could be observed in this polymer we conducted SAXS experiments on a small oriented sample that was produced by plane strain compression of pieces from a compression molded plaque of an industrial grade resin. In our view orientation texture aids microstructural identification by lifting the degeneracy that is present in isotropic materials.

Figure 3 shows portions of the scattering patterns obtained at temperatures of 35 °C, 80 °C, and 147 °C, together with the difference between the 147 °C and the 80 °C patterns. The scattering pattern at 35 °C does not exhibit any of the kind of contrast that is normally associated with scattering from lamellar stacks. The pairs of spots in the 80 °C and 147 °C patterns demonstrate the TICV effect due to the divergence in electron density between the amorphous and crystalline components of the lamellar microstructure that sets in at approximately 65 °C. The value of  $T_g$  for P4MP is somewhat ambiguous [7], so that further measurements using the TICV method might serve to define it more closely.



**Figure 3.** - 2-D SAXS patterns for P4MP. See text for meaning of labels.

In these patterns the scattering at low  $q$  is very weak. The “matrix scattering” for this material is basically that which is seen in at 35 C in Figure 3. This stands in sharp contrast to the data from sPS[1], so that it is reasonable to conjecture that the molecular architecture of the polymer has a strong effect on the matrix scattering. Other factors such as processing conditions, the existence of voids or other inclusions, etc. should also be considered when interpreting the matrix scattering.

It is interesting to note that there is essentially no low  $q$  scattering whatsoever in the difference pattern. This effectively confirms the argument of Schultz[8] that the scattering usually observed at the lowest scattering angles in semicrystalline polymers should be attributed to causes other than the lamellar microstructure.

Detailed characterization of lamellar microstructures is often carried out using correlation function analyses[9]. Our observations suggest that difference patterns obtained using the TICV procedure may provide better inputs to correlation function analyses because the difference patterns are relatively free of interfering effects.

### Conclusions

The two examples of the TICV method shown above are meant to be illustrative rather than quantitative. The method must be applied to a wider variety of semicrystalline polymers in order to characterize its sensitivity. A wider range of microstructural types including block copolymers and amorphous polymers should be subjected to the method in order to determine whether it is useful for characterizing other aspects of polymer microstructure.

Data not reported here demonstrate that the TICV method works well in a synchrotron SAXS environment provided that the variations in incident flux can be properly accounted for. The enhanced incident flux allows for more rapid temperature scans with some improvements in signal to noise ratio. Experiments applying the TICV method in a SANS environment are currently underway. The method may be especially useful for chlorinated and fluorinated industrial polymers for which strong absorption creates problems in SAXS measurements.

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