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Polyamide 6 – the trouble with crystal polymorphism

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Polyamide 6 (PA6) is one of the most popular semi-crystalline engineering thermoplastics polymer having excellent chemical stability and mechanical strength. One of the most remarkable features of PA6 is that, depending on thermo-mechanical or chemical treatment, it crystallizes in different crystal types.

Exploring the existing in literature "crystal form space" of PA6, one finds two well resolved and documented polymorphs, i.e. the α- and the γ-form [1.2]. Basically, both structures consist of hydrogen-bonded sheets with fully extended chains. Besides these crystal structures, depending on the thermal history, another molecular arrangement, known as a β–form, can co-exist with the α–form. The β–form is characteristic for poorly crystalline samples [3,4]. Furthermore, a plethora of other polymorphs of PA6 are described in literature, for example γ* [5,6], pleated α [7], paracrystalline monoclinc α, and nematic (pseudo)hexagonal γ [8]. It is widely accepted that these unstable forms can be transformed into the α-form using suitable thermal treatment [9,10]. In contrast, the γ- to α-form transition cannot take place, unless we employ reagents being able to interact with the hydrogen bonds, or unless we treat the sample at temperatures higher than its melting point [9].

The Differential Scanning Calorimetry (DSC) output of PA6 involves a multitude of thermal events. Specifically, the number of endotherms depends on the previous thermal history and heating rate. Understanding the crystallization behavior of PA6 (and other polymers) is often related to understanding of its melting mechanism. It is common to first introduce a defined thermal history to a sample and then, on the basis of the melting results, attempt is made to explain the crystallization process.

In this it work it is explained that such attempt should be made with care. The structural changes occurring to PA6 samples during heating after different thermo-chemical treatment are extracted from synchrotron Wide-Angle X-ray Diffraction experiments (WAXD) and are discussed in the context of parallel DSC data. The results reveals that:

- the β–form precedes the α–form upon cooling from quiescent melt;
- the X-ray diffraction patterns of the β–form are different from those of the γ–form;
- the thermal behavior of the β–form is different from those of the γ–form.

These results, being contradictory to the conventional wisdom, shows that due to crystalline polymorphism of PA6, interpretation of melting behavior revealed by DSC is not straightforward and should only be done when morphology sensitive techniques, like synchrotron X-ray diffraction, are used in conjunction with DSC. Besides the synchrotron experimental issues of this work are discussed as well.

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[1] D. R. Holmes, C. V. Bunn, D. J. Smith, *J. Polym. Sci*. **17** (1955) 159.
[2] H. Arimoto, M. Ishibashi, M. Hirai, Y. Chatani, *J. Polym. Sci.,Part A* **3** (1965) 317.
[3] I. Sandeman, A. Keller, *J. Polym. Sci*. **19** (1956) 401.
[4] A. Ziabicki, *Kolliod-Z.* **167** (1959) 132.
[5] K. H. Illers, *Makromol. Chem.* **179** (1978) 497.
[6] K. H. Illers, H. Haberkorn, P. Simák, *Makromol. Chem*. **158** (1972) 285.
[7] R. F. Stepaniak, A. Garton, D. J. Carlsson, D. M. Wiles, *J. Polym. Sci., Polym. Phys. Ed*. **17** (1979) 987.
[8] L. G. Roldan, H. S. Kaufman, *Polym. Lett*. **1** (1963) 603.
[9] J. P. Parker, D. H. Lindenmeyer, *J. Appl. Polym. Sci*. **21** (1977) 821.
[10] J. Gianchandani, J. E. Spruiell, E. S. Clark, *J. Appl. Polym. Sci*. **27** (1982)3527.