SIMULTANEOUS SMALL-ANGLE X-RAY SCATTERING
AND WIDE-ANGLE X-RAY DIFFRACTION
A powerful new technique for thermal analysis

A. J. Ryan

MANCHESTER MATERIALS SCIENCE CENTRE UNIVERSITY OF MANCHESTER AND
UMIST, GROSVENOR STREET, MANCHESTER, M1 7HS, UK

The simultaneous SAXS/WAXD technique is shown to provide an unambiguous method for following structural changes taking place during the programmed heating of a range of multiphase polymeric materials. Results are given for polyethylene, block copolyurethanes and block copolyesters containing liquid crystalline hard segments.

Keywords: morphology of multiphase polymers, small-angle X-ray scattering (SAXS), wide-angle X-ray diffraction (WAXD)

Introduction

The experimental technique of DSC or DTA is often used in the thermal characterisation of structure-property-relations in polymers [1]. The phenomena investigated, such as melting and glass transitions in semi-crystalline polymers or the glass transitions of blends, are associated with strong morphological features. Much of the knowledge concerning the crystallisation of polymers comes from the application of programmed heating and cooling, and isothermal crystallisation, studies by DSC combined with post-mortem assessment of morphology by either X-ray diffraction or microscopy [1]. Similarly, the existence of phase separation in polymer blends [2] or microphase separation in block copolymers [3] is often assessed by DSC with confirmation sought by scattering, microscopy and dynamic mechanical thermal analysis. The kinetics of (micro)phase separa-
tion can be followed by DSC but the thermal response is weak and these experiments are often semi-quantitative [4]. In recent years DSC has been applied to the characterisation of transitions in liquid crystalline materials. The transition from the crystalline to nematic to isotropic phases has been deduced from DSC and microscopy studies on thermotropic polyesters [5]. More recently the complex phase behaviour of block copolymers with liquid crystalline segments has been investigated via parallel DTA and X-ray experiments in order to map out phase diagrams [6].

The technique of wide-angle X-ray diffraction (WAXD) may be used to solve the crystal structure if the full diffraction pattern of a single crystal or fibre is available [7]. Due to the polycrystalline nature of most polymers it is more common to obtain the one-dimensional, 1-D, powder diffraction pattern and, wherever possible, index the structure from this. For example the two crystalline forms of polyethylene can be readily distinguished from their powder diffraction patterns [8].

Small angle X-ray scattering (SAXS) is a well established technique for studying the morphology of multiphase polymers [8]. X-rays are scattered by regions with different electron densities. It is often used in tandem with DSC to study polymer crystallisation and microphase separation in block copolymers. Information is obtained in the form of a scattering pattern; as with WAXD un-oriented materials have 1-D patterns which can be analysed using Bragg’s law leading to information on the structural features with size-scales from 50–1000 Å. For liquid crystalline and semi-crystalline polymers this corresponds to the crystallite size, for block copolymers the unit cell. In some cases, where the data are of a very high statistical quality (i.e. a high signal to noise ratio), correlation function analyses can yield further spatial information such as the thickness of the interface between microphases in a block copolymer or between the crystalline and amorphous regions of a semicrystalline polymer [8].

Conventional SAXS and WAXD experiments, i.e. those utilising sealed-tube or rotating anode X-ray sources, are limited to stable materials due to the long times (hours) required to obtain patterns of sufficient statistical quality. Patterns may be taken as a function of temperature but generally this is not done due to the difficulties of furnace design. Furnaces must generally contain vertical windows that will support molten polymers and be transparent to X-rays; suitable materials are mica and crosslinked polyimide. The major problem is with leakage after long times at high temperatures, and subsequent camera contamination. To obtain statistically significant SAXS and WAXD patterns at heating rates used in DTA or DSC experiments (time resolution of less than one minute and preferably less than one second), the high flux of synchrotron radiation and fast, position-sensitive, electronic detectors must be used. Synchrotron radiation is produced at special facilities (such as the Stanford Synchrotron Radiation Laboratory (SSRL) at

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