

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

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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-

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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

Stanford, California and the Synchrotron Radiation Source (SRS) at Daresbury, UK) by maintaining electrons in a relativistic orbit; the radiation is taken off at ports which are at a tangent to the ring; the radiation is essentially point focussed and forward-collimated white light, monochromators and focussing optics are then used to optimise the light source for each experiment. There are around twenty suitable synchrotrons worldwide each containing up to sixty beamlines.

The combined techniques of DSC/SAXS and DSC/WAXD were pioneered by Koberstein and Russell [9] using synchrotron radiation (SSRL) as the X-ray source and a Mettler FP-85 DSC which had been modified to allow transmission of radiation beams. Experiments on low density polyethylene, a well characterised material, were performed in order to validate the technique. A large contribution to the understanding of the complex behaviour of thermoplastic copolyurethanes has been made by detailed study using DSC/FTIR [10], DSC/SAXS [11, 12] and DSC/WAXD [13] by Koberstein and coworkers. The thermoplastic copolyurethanes studied comprise semi-crystalline aromatic urethane hard segments ($T_g \approx 100^\circ\text{C}$; $T_m \approx 220^\circ\text{C}$) covalently bonded to amorphous polyether soft segments ($T_g \approx -60^\circ\text{C}$); the materials are strongly microphase-separated at their service temperature. The properties obtained for a given composition are strongly dependent on thermal history, as the microphase separation transition and the maximum rate of hard segment crystallisation coincide at $\approx 160^\circ\text{C}$. The micro-structure of the polymer may evolve by at least four routes. Considering the behaviour of a 50% hard segment material, at high temperatures ($>240^\circ\text{C}$) the copolymer is homogeneous. If it is quenched rapidly to below the T_g of the mixture ($\approx 10^\circ\text{C}$) a homogeneous glass is obtained. When quenched to below the hard segments T_g then a microphase-separated structure evolves with amorphous hard segments (the amorphous HS may then crystallise on further heating). Slow quenching to just below the microphase separation transition allows hard-segment crystallisation to complement microphase separation. A shallow quench to just below the hard segments T_m causes crystallisation to occur from solution. The morphologies formed and the kinetics of their formation have been deduced by separate DSC/SAXS and DSC/WAXD experiments. The inevitable conclusion of Koberstein's work is that combined SAXS/WAXD is a step toward minimising experimental effort and realising unambiguous results by removing the need for repeated experiments on different samples.

Ungar and Feijoo [14] have also used DSC/SAXS and DSC/WAXD (using SRS as the radiation source and a modified Mettler FP85) to study chain folding in the crystallisation of high molecular weight, monodisperse, linear alkanes and the morphological transitions of side chain liquid crystalline polymers. The need for simultaneous SAXS/WAXD is also borne out by this work.

Zachmann [15] made the first attempt at combining WAXD and SAXS to study PET and its related liquid crystalline polymers. Due to the experimental ar-

rangement used the data had a poor signal to noise ratio at DSC heating rates. This pioneering work cannot be ignored, despite the limitations of the signal to noise ratio in calculating phase compositions, good spatial information was obtained.

Description of the experimental arrangement at SRS, Daresbury

Simultaneous SAXS/WAXD measurements have been recently made on beamline 8.2 on SRS at the SERC Daresbury Laboratory, Warrington, UK. The white radiation from the bending magnet is monochromated by a cylindrically bent GE(111) monochromator with an asymmetric cut of 10.5° and a horizontal compression ratio of 13:1 for the incoming beam. The distance from the tangent point of the storage ring to the monochromator is 20.0 m. The horizontal acceptance of the monochromator is approximately 5 mrad. The alignment is such that 1.52 \AA radiation is selected. An uncoated, fused-quartz, mirror receives the monochromated radiation under a glancing angle of about 4 mrad. The mirror, which is cylindrically bent and 0.7 m in length, effectively cuts off all of the higher harmonics transmitted by the monochromator and focuses the radiation in the vertical plane. By varying the bending radius of the mirror, the radiation can be focussed in the horizontal plane in the range of 0.2 to 4.5 m behind the sample stage. The beamline is kept under high vacuum and four sets of slits are used for beam size definition. A highly collimated beam is produced with a typical cross section of $0.3 \times 4 \text{ mm}^2$ in the focal plane. With the SRS operating at 2 GeV and 200 mA a flux of 4×10^{10} photons s^{-1} is generated at the sample position.

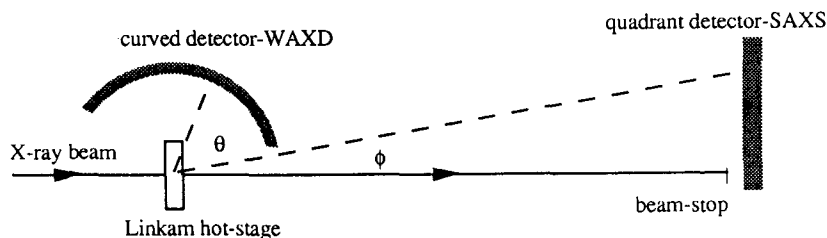


Fig. 1 Schematic of the simultaneous SAXS/WAXD camera geometry

The camera is equipped with a multiwire quadrant detector (SAXS) located 3.5 m from the sample position and a curved knife-edge detector (WAXD) that covers 120° of arc at a radius of 0.4 m. A schematic diagram of the camera geometry is given in Fig. 1. The gap between the sample and the WAXD curved knife-edge detector is open to the atmosphere. Only 40° of arc are active in

these experiments; the detector has a spatial resolution of $50\ \mu\text{m}$ and can handle up to $\sim 100\ 000\ \text{counts}\cdot\text{s}^{-1}$. A helium chamber is placed between the sample and SAXS detector in order to reduce air scattering and absorption. Both the exit window of the beam-line and the entrance window of the helium chamber are made from $15\ \mu\text{m}$ mica, and the exit window of the helium chamber is made from $10\ \mu\text{m}$ Kapton film. A beamstop is mounted just before the exit window to prevent the direct beam from hitting the SAXS detector which measures intensity in the radial direction (over an opening angle of 70° and an active length of $0.2\ \text{m}$) and is only suitable for isomorphous scatterers. It has an advantage over single-wire detectors in that the active area increases radially improving the signal to noise ratio. The spatial resolution of the SAXS detector is $500\ \mu\text{m}$ and it can handle up to $\sim 250\ 000\ \text{counts}\cdot\text{s}^{-1}$.

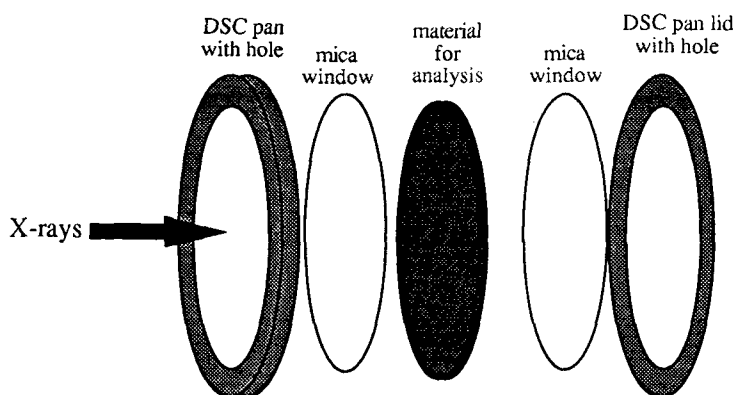


Fig. 2 Modified DSC pan used as sample holder for SAXS/WAXD experiments

The specimens for SAXS/WAXD were prepared by placing disks, $1\text{--}2\ \text{mm}$ thick and $\approx 8\ \text{mm}$ diameter, cut from compression moulded sheets, in a cell comprising a DuPont DSC pan fitted with windows ($\approx 7\ \text{mm}$ diameter) made from $5\ \mu\text{m}$ thick mica. The modified DSC pans are illustrated in Fig. 2. Loaded, sealed pans were glued to a J-type thermocouple and placed in a spring-loaded holder in a Linkam hot-stage mounted on the optical bench. The silver heating block of the hot-stage contains a $4\times 1\ \text{mm}$ conical hole which allows the transmitted and scattered X-rays to pass through unhindered. A nominal heating rate of $3\ \text{deg}\cdot\text{min}^{-1}$ was used. Due to the nature of the furnace there was a temperature drift across the sample chamber which required direct measurement of temperature at the sample position over and above the temperature monitoring and control of the furnace.

The scattering pattern from an oriented specimen of wet collagen (rat-tail tendon) was used to calibrate the SAXS detector and aluminium was used to calibrate the WAXD detector. Parallel plate ionisation detectors placed before and

after the sample cell record the incident and transmitted intensities, thus enabling changes in the specimen attenuation factors (a function of transmission and thickness) to be monitored continuously. The experimental data were corrected for background scattering (subtraction of the scattering from the camera, hot stage and an empty cell), sample thickness and transmission, and the positional alinearity of the detectors.

The general requirement of these experiments is to have one diffraction pattern per two degrees centigrade. The performance of the experimental arrangement gave a time resolution of 1 second for positional data, this would allow heating rates of up to $120 \text{ deg}\cdot\text{min}^{-1}$. Time resolution of 1 minute was required for calculation of correlation functions and interfacial thicknesses, which limits the heating rates to $<2 \text{ deg}\cdot\text{min}^{-1}$.

Results

Polyethylene

The annealing and melting of a well-characterised sample of high density polyethylene (HDPE) was chosen as the experiment to commission and validate the simultaneous SAXS/WAXD camera. The most dramatic way of displaying the data is as three-dimensional surface plots of angle vs. intensity vs. temperature; however, this takes up enormous amounts of space and only a limited number of diffraction patterns and some analysed data will be presented here.

The initial form of the data is a plot of intensity (I) vs. scattering vector (q); although there is a peak in the intensity curve the lamellar nature of polyethylene crystals means that the Lorentz correction (q^2) must be applied to the intensity

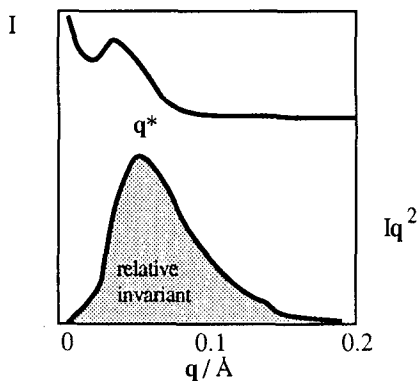


Fig. 3 Typical SAXS data for a semicrystalline sample of HDPE. Upper curve intensity, I , vs. scattering vector, q ; lower curve Lorentz corrected intensity, Iq^2 , vs. scattering vector, q

before spatial information is extracted. This is illustrated schematically in Fig. 3 and shows the shift to larger scattering vectors caused by application of the Lorentz correction. The peak in the Lorentz corrected scattering curve (q^*) may be analysed according to Bragg's law ($d = 2\pi/q^*$) to derive the d -spacing. The invariant (Q) is a linear function of the electron density difference between the amorphous and crystalline phases $\langle \eta^2 \rangle$ and is obtained from the integral

$$\langle \eta^2 \rangle = \frac{Q}{2\pi i_e} = \frac{1}{2\pi i_e} \int_0^\infty I(q) q^2 dq$$

where i_e is the Thompson scattering factor. The quantity Q is known as the invariant being independent of the size or shape of the structural heterogeneities. The absolute value of the invariant requires absolute intensity measurements, thermal background subtraction, and extrapolation to $q = 0$ and ∞ and is computationally difficult to achieve. The major contribution to the experimental invariant can be used to characterise structure development, such as the degree of crystallisation or microphase separation, and is readily assessed by Simpson's rule integration of the shaded area in the Iq^2 vs. q curve of Fig. 3; this is referred to as the relative invariant.

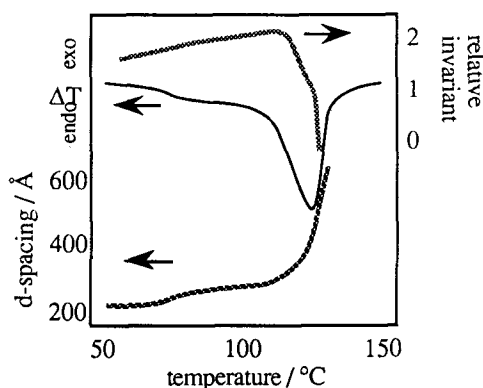


Fig. 4 Comparison of relative invariant (upper curve), DSC trace (middle curve) and d -spacing (lower curve), as a function of temperature for HDPE

Programmed heating experiments were performed at a heating rate of $2.8 \text{ deg}\cdot\text{min}^{-1}$ from room temperature to 150°C . The d -spacing and relative invariant data have been calculated and are illustrated along with the corresponding DTA curve in Fig. 4. As the polymer is heated the d -spacing increases as the material expands, at $\approx 80^\circ\text{C}$ a more rapid increase in the d -spacing occurs as some lamella crystals begin to thicken and some small imperfect crystallites melt, the

d -spacing then increases with the volume change on heating. Up to the melting point of 138°C the invariant shows a nearly linear increase with temperature which is a result of the increased density difference between the crystalline and amorphous regions. At the onset of crystalline melting there is a sharp drop in the invariant and an increase in the observed d -spacing (this is because individual lamella crystallites melt and so the apparent correlation distance increases); the melting point may be estimated either by drawing tangents or taking the second derivative of the curves. There is a good agreement between the onset of melting by DTA and SAXS.

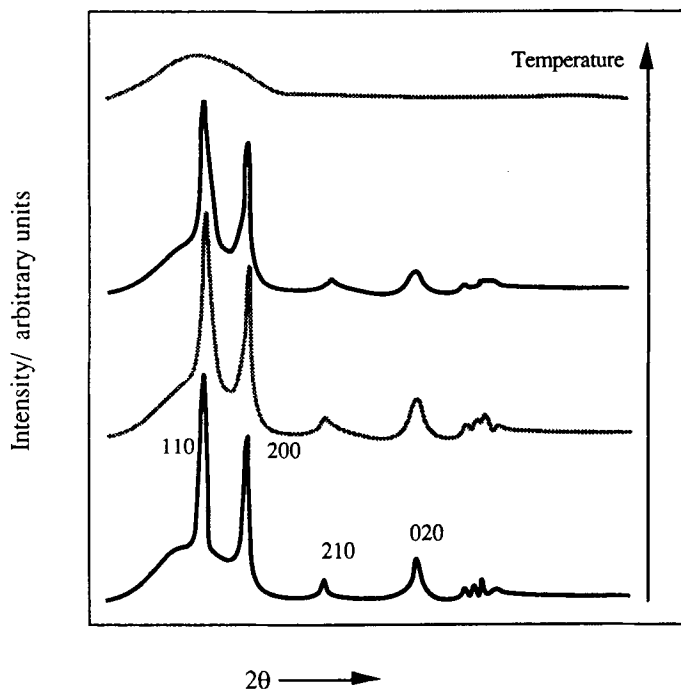


Fig. 5 WAXD patterns of HDPE as a function of temperature. Numbers next to the peaks on the lowest curve correspond to the Miller indices of the orthorhombic crystal

The corresponding WAXD data are shown in Fig. 5. Qualitatively there are changes in the diffraction patterns which correlate with the SAXS and DTA data. The lower dotted curve represents the shape of the diffraction patterns in the temperature interval 80° to 120°C where the crystallites are at their largest. The lower solid curve represents a diffraction pattern ten degrees below the melting point and shows the broadening of the reflections due to softening of the crystal and melting of some crystallites and other crystals thickening as the melting point

is approached; the upper dashed curve illustrates further line-broadening and a reduction in intensity, until at two degrees above the melting point the diffraction pattern has transformed into that of an amorphous liquid. Generally the simultaneous SAXS/WAXD on polyethylene confirm, in one unambiguous experiment, the generally held understanding of crystalline melting in polyethylene. Crystal thickening competes with the first order melting of individual crystallites and the distribution of crystallite size causes a distribution in melting points and this is observed as a broad melting range.

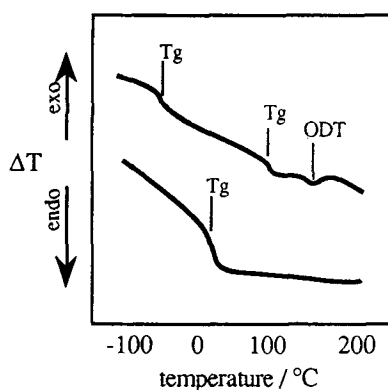


Fig. 6 DTA traces for a polyurethane with amorphous hard segments. Upper curve, first run; lower curve, second run after quenching into liquid nitrogen

Quantitative analysis of the WAXD data requires the measurement of full width at half maximum height. The degree of crystallinity can be calculated from WAXD patterns by subtraction of the scattering from the amorphous material, integrating for the area under the peaks and dividing by the corresponding area for a fully crystalline standard. These analyses are beyond the scope of this paper and will be published elsewhere [16].

Polyurethanes

The temperature-dependence of the thermal, rheological and morphological properties of block copolyurethanes have also been studied [17]. Two materials were investigated; one comprised amorphous hard segments formed from a 50:50 w:w mixture of 4,4' and 2,4'-diphenylmethane diisocyanate and 1,4-butane diol, and soft segments based on a poly(oxyethylene-block-oxypropylene) diol of molecular weight 2300; the second material comprised semi-crystalline hard segments formed from 4,4'-diphenylmethane diisocyanate and 1,4-butane diol, and soft segments based on the same polyether diol.

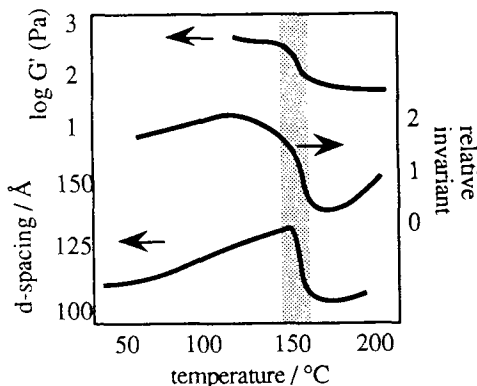


Fig. 7 Comparison of in-phase shear modulus G' (upper curve), relative invariant (middle curve), and d -spacing (lower curve), as a function of temperature for a polyurethane with amorphous hard segments

For the material with amorphous hard segments, DTA curves, (Fig. 6) confirmed the existence of a microphase-separated structure in the copolymer which exhibited two glass transitions (-45° , 100°C); material quenched from above a third weak transition (ODT) was homogeneous and showed only one intermediate glass transition. Dynamic mechanical analysis confirmed the glass transition behaviour and showed a drop in modulus, G' , at elevated temperatures which was ascribed to the order-disorder transition of the micro-phase separated block copolymer. Intensity-scattering vector data obtained in real-time small angle X-ray scattering experiments showed a strong Bragg reflection at low temperatures which became much less intense (reducing the relative invariant) and shifted to higher angles at elevated temperatures. The changes in the scattering peak occurred in the same temperature interval (Fig. 7, shaded area) as the thermal and dynamic mechanical transitions, and were ascribed to the order-disorder transition [17].

For the material with semi-crystalline hard segments the DTA curve (Fig. 8) also showed the existence of a microphase-separated structure in the copolymer which exhibited a low temperature glass transition ($T_g \approx -50^\circ\text{C}$) and high temperature ($T_m \approx 170^\circ$, 200°C) multiple melting. The d -spacing and relative invariant data from the SAXS part of the relevant simultaneous SAXS/WAXD experiments are included for the first run. A strong SAXS reflection is observed at low temperatures ($< 100^\circ\text{C}$) which decreases in intensity (reducing the relative invariant) and shifts to lower angles (an increase in the d -spacing) as the multiple melting transitions occur. Morphology formation in polyurethanes is complex, the semicrystalline hard segment is fractionated by sequence length during ordering. During programmed heating individual crystallites melt and immediately dis-

solve in the soft segment increasing the observed correlation length, the d -spacing. The degree of crystallinity from WAXD qualitatively followed the changes in the relative invariant.

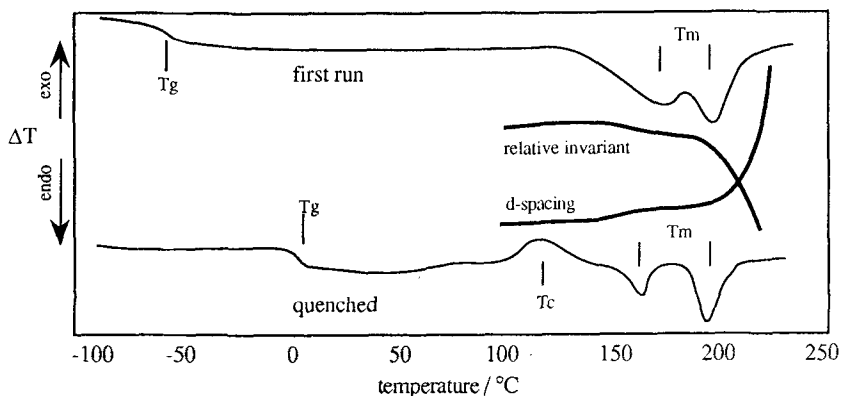


Fig. 8 Comparison of DTA traces (first run and quenched) and the derived SAXS data (relative invariant and d -spacing), as a function of temperature for a polyurethane with semi-crystalline hard segments

Material quenched into liquid nitrogen from above the melting transition exhibits an intermediate glass transition ($T_g = 5^\circ\text{C}$), cold crystallisation ($T_c = 130^\circ\text{C}$) and multiple melting ($T_m \approx 165^\circ, 190^\circ\text{C}$). Due to problems of maintaining materials at liquid nitrogen temperatures during experiment preparation it is not possible to perform simultaneous SAXS/WAXD experiments from low temperatures on the quenched polyurethanes. They showed a strong SAXS reflection at room temperature which showed similar behaviour to the first run and disappeared at the highest DTA melting point. The WAXD data were complex and showed evidence of melting and recrystallisation, the changes in the degree of crystallinity did not correlate with the relative invariant indicating the existence of amorphous hard segments.

The competition between the crystallinity of the hard segments and the thermodynamics of the block copolymer may be deduced from the analysis of DTA and SAXS/WAXD experiments. The semi-crystalline hard segments stabilise the microphase separated morphology to temperatures in excess of the thermodynamic order-disorder transition observed for the material with the amorphous hard segments. In the polyurethane with amorphous segments the order-disorder transition is observed as a decrease in d -spacing as the segments relax from stretched conformations in the ordered state. In the polyurethane with semicrystalline segments the d -spacing increases as individual lamella crystals melt and dissolve at temperatures in excess of the order-disorder transition. Fur-

thermore the morphology and degree of crystallinity of the hard segments was strongly dependent on thermal history, this is in agreement with Koberstein [12, 13].

Summary and conclusions

The simultaneous SAXS/WAXD technique has been shown to provide an unambiguous method for following the structural changes taking place during programmed heating in a range of multiphase polymeric materials. The demand for synchrotron radiation is high, so performing simultaneous experiments has an obvious advantage. In the next series of experiments programmed cooling and isothermal annealing following a quench will be investigated on the materials discussed here. Plans are also in hand to replace the Linkam hot-stage with a purpose-built DTA. Finally, the application of the SAXS/WAXD technique to other areas of materials science, such as structure-development during reaction injection moulding of polymers and composites [18], sol-gel processing of ceramics, or solidification in metal alloys, is also possible.

* * *

The simultaneous SAXS/WAXD camera was built by Wim Bras, Neville Greaves and Gareth Derbyshire at Davesbury. The data collection and analysis were conducted by the author, Wim Bras, Gareth Derbyshire, Andrew Felton, Steven Naylor and Saria Benadda.

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Zusammenfassung — Es wird eine simultane SAXS/WAXD-Technik vorgestellt, um eine eindeutige Methode zur Verfolgung von Strukturänderungen bei programmiertem Aufheizen einer Reihe von polymeren Mehrfachphasenstoffen zu entwickeln. Darüberhinaus werden Ergebnisse zur Anwendung bei Polyethylen, Blockmischpolyurethanen und Blockmischpolyestern mit flüssig-kristallinen Hartsegmenten beschrieben.