

angular widths of approximately  $60^\circ$ . In order to collect a complete diffraction dataset a range of rotation of  $180^\circ$  was required. Physical sample restrictions limited data collection to a range of  $120^\circ$  but due to the large angular width of the reflections, reciprocal lattice points occurring in the 'physical blind region' had associated reflections which were visible within our range of rotation and could be fitted by extrapolation of the recorded data. Figure 4 shows data collected on the equator at sample rotations ranging from  $-60^\circ$  to  $+60^\circ$  in increments of  $10^\circ$ . The data recorded during this neutron fibre diffraction experiment are in the process of analysis at the present time. The data recorded are expected to reveal a more detailed picture of B-DNA hydration.

## References

- [1] Langan, P., *et al*, *J. Appl. Cryst.*, (1996) (in press)
- [2] Rupprecht, A., *Biotech. Bioeng.*, **7**, 93, (1973)
- [3] Denny, R.C. (in preparation)
- [4] Arnott, S., Hukins, D.W.L., *Biochemical and Biophysical Research Communications*, Vol. **47**, No. 6, 1504-1510, 1972
- [5] Drew, H.R., Dickerson, R.E., *J. Mol. Biol.*,

## Chain Conformations in Polyurethanes : A SAXS & SANS Study

A.J. Ryan<sup>1,2</sup>, S. Naylor<sup>1</sup>, N.J. Terrill<sup>1</sup>, S. King<sup>3</sup>

1 UMIST Materials Science Centre

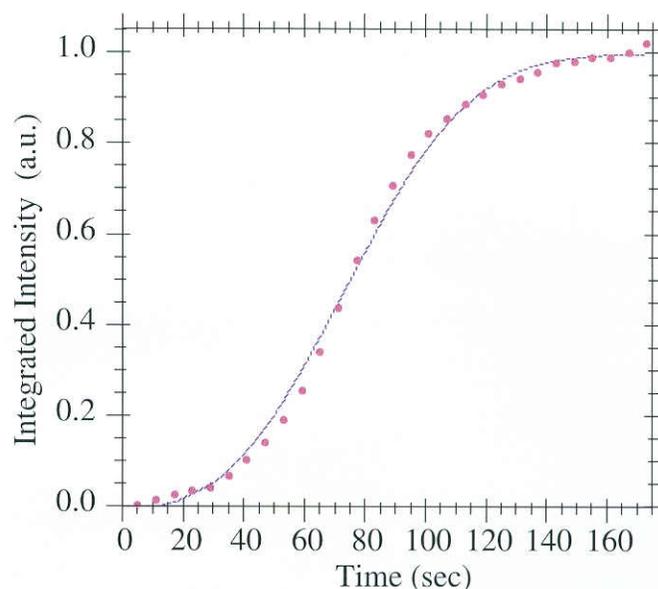
2 CCLRC Daresbury Laboratory

3 CCLRC Rutherford Appleton Laboratory

Segmented polyurethanes are statistical block copolymers comprising incompatible hard and soft blocks. A range of poly(ether-urethane) copolymers have been synthesised in order to verify which is the primary driving force behind microphase separation: block incompatibility or crystallisation of the segments. Two classes of copolymer have been synthesised: one class contained a semi-crystalline 4,4'-methylene diphenyl diisocyanate (4,4'-MDI) and butanediol (BDO) based hard segment, the other contained an amorphous hard segment based on a blend of 2,4- and 4,4'-methylene diphenyl diisocyanate (2,4/4,4'-MDI) and BDO. The soft segment in both types of copolymer was polypropylene oxide (PPO). The materials were synthesised with various hard segment contents: 25, 50 and 75 % by weight. The PPO samples had

molecular weights that ranged from 400 to 4000.

Characterisation of the materials involved heating the materials until homogeneous in order to remove all traces of prior thermal history, and then annealing the samples at different temperatures. Quenching in liquid nitrogen was used to "freeze-in" the resultant morphologies. These samples were then analysed using separate differential thermal analysis experiments (DTA) and X-ray scattering experiments. Both the 4,4'-MDI and 2,4/4,4'-MDI copolymers which contained low hard segment contents or low molecular weight soft segments were shown to be homogeneous after annealing. Annealing had little effect on these materials. However, annealing the higher molecular weight 4,4'-MDI copolymers promoted crystallisation and produced larger microdomains with sharper interfaces. As a consequence of this, the PPO chains were stretched more in the 4,4'-MDI copolymers than in the 2,4/4,4'-MDI materials. In contrast, annealing had little effect on the 2,4 / 4,4'-MDI copolymers, evidence that crystallisation plays an

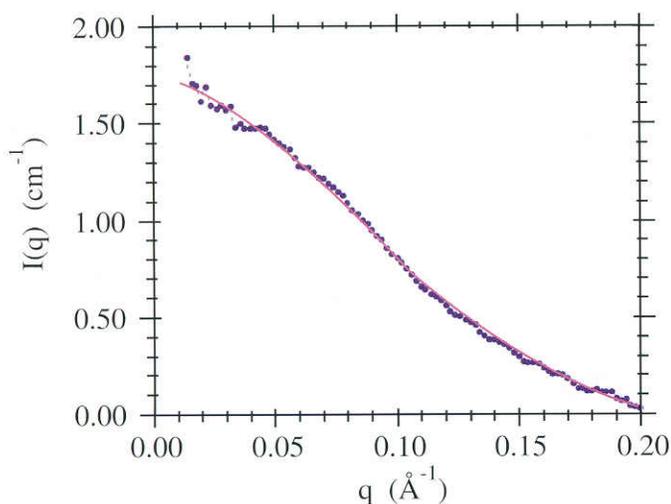


**Figure 1** Integrated intensities during the isothermal microphase separation of a polyurethane. The line is a fit of the Avrami model to the data.

important part in the microphase separation process. The kinetics of microphase separation and crystallisation were investigated using time-resolved X-ray scattering experiments. Several models were used, including Avrami and time-dependent Ginzburg-Landau (TDGL) analysis. Aspects of the microphase separation process fitted both the spinodal decomposition (SD), and nucleation and growth (NG) models. However, the latter was favoured because the Avrami equation was seen to be in excellent agreement with the data (see Figure 1),

and fitted the data better than the SD models. The thermal history of the 4,4'-MDI materials was observed to have an important effect on the melting behaviour of the samples, possible causes being chain branching and side-reactions.

Changes in the conformation of the PPO soft segment were investigated using small-angle neutron scattering (SANS). A phase contrast matched copolymer was used to measure changes in the radius of gyration of the soft segment with temperature in a semi-crystalline, microphase-separated material. The Debye model fitted the data well (see Figure 2), and showed the soft segments to be initially in somewhat extended conformations, as a result of chain stretching brought on by movement of the hard

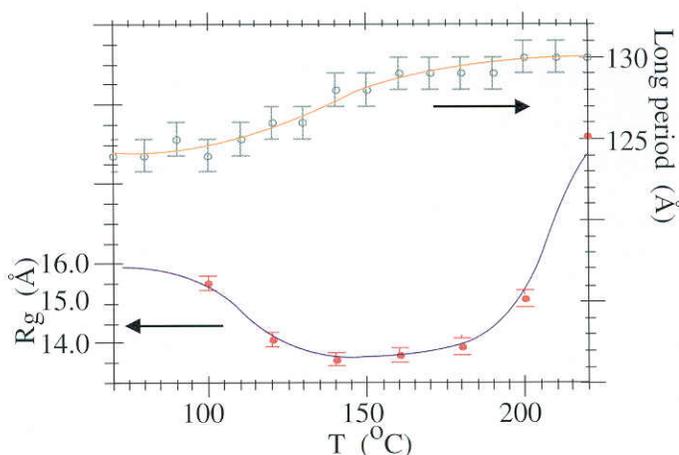


**Figure 2:** Fit of the Debye Model to the SANS data for a contrast matched material.

segments during microphase separation / crystallisation.

On heating, some disordering occurred as the soft segments began to pull hard segments out of the domains, to take the form of random coils. In addition, SANS patterns from hydrogenous polymers showed excellent agreement with SAXS patterns, confirming that the microdomains present in the microphase separated materials were the scattering entities in both techniques, and provided confidence in the spatial information so obtained.

Changes in the long period, obtained using correlation function analysis on SAXS data for a hydrogenous copolymer, correlated well with changes in the SANS data obtained for the contrast matched equivalent. The sample was shown to begin to disorder on softening at  $\approx 100^\circ\text{C}$  and was mostly phase mixed by  $180^\circ\text{C}$  with some isolated crystalline



**Figure 3:** Variation in the long period, from SAXS, and the  $R_g$  of the soft segment, from SANS, as a function of temperature.

domains present. At  $\approx 200^\circ\text{C}$  these larger domains melted as the material became homogeneous.

As the temperature is increased, the radius of gyration of the soft segment initially decreases. This occurs because the retractive forces exerted by the soft segment increase with temperature, and consequently pull some hard segments out of the hard domains, so that the soft segments relax into smaller random coils. At higher temperatures, phase mixing begins to take place, leading to an increase in  $R_g$  as a result of interactions between the hard and soft segments, much as a homopolymer is swollen by a good solvent. The segments still take the form of random coils but are somewhat extended. The long period spacing  $L_p$  increases steadily with temperature once the material begins to soften at  $\approx 100^\circ\text{C}$ , until a temperature of  $160^\circ\text{C}$  is reached, when the long spacing remains relatively constant at  $129\text{Å}$ . This behaviour may be attributed to the preferential melting of smaller crystalline domains: hard blocks containing a lower number of MDI-BDO residues will begin to melt first, from simple thermodynamic considerations. As these hard blocks melt, the soft segments attached to them will relax into random coils, and this is reflected in the observed decrease in  $R_g$ . At this point the sample resembles a mixed phase matrix with isolated large crystalline domains distributed throughout, *i.e.*, the sample is mostly disordered but retains some crystallinity. A further increase in  $L_p$  and  $R_g$  is observed at  $\geq 200^\circ\text{C}$ , when the remaining hard domains begin to melt.

The experimental studies confirmed the domination of crystallisation over microphase separation due to

### Structural Studies of Helical Poly( $\beta$ -L-Aspartate)s

C.Aleman, F.Lopez-Carrasquero, J.J.Navas,  
M.Garcia-Alvarez, S.Leon and S.Munoz-Guerra

Department d'Enginyeria Quimica, E.T.S.I.I.B., Universitat  
Politecnica de Catalunya

Poly( $\beta$ -L-aspartate)s are nylon 3 derivatives with an alkoxy carbonyl group stereoregularly attached to the backbone  $\beta$ -carbon atom of every repeating unit:  $[\text{NHCH}(\text{COOR})\text{-CH}_2\text{-CO-}]$ . This family of compounds is able to crystallise in helical structures with features similar to the  $\alpha$ -helix characteristic of polypeptides. More specifically, poly( $\alpha$ -isobutyl- $\beta$ -L-aspartate) constitutes the first example of a nylon derivative taking up helical conformations traditionally restricted to polypeptides and proteins [1]. On the other hand, it is a well known feature that in polypeptides, in particular in poly( $\beta$ -alkyl- $\alpha$ -L-aspartate)s, minor modifications in the side chain may give rise to changes in the conformational parameters or may even reverse the handedness of the helix [2]. Consequently, a detailed study of the influence of the side group R on the helical structures of poly( $\beta$ -L-aspartate)s is highly desirable.

In this work we examined the helical structures of six polymers:

- I. poly( $\alpha$ -methyl- $\beta$ -L-aspartate);
- II. poly( $\alpha$ -ethyl- $\beta$ -L-aspartate);
- III. poly( $\alpha$ -propyl- $\beta$ -L-aspartate);
- IV. poly( $\alpha$ -n-butyl- $\beta$ -L-aspartate);
- V. poly[ $\alpha$ -(2-methoxyethyl)- $\beta$ -L-aspartate];
- VI. poly( $\alpha$ -cyclohexyl- $\beta$ -L-aspartate).

The crystal structures of such compounds were characterised by X-ray diffraction of fibres and films. Molecular models corresponding to such structures were determined by combining two well-established methodologies. Firstly, a conformational analysis using energy calculations was performed in order to find the more favourable molecular models. Secondly, such models were refined against X-ray diffraction data with the Linked-Atom Least-Squares (LALS) methodology.

A hexagonal crystal form was found for the six compounds under study. It is composed of 17/4-helices for the methyl and ethyl derivatives and of 13/4-helices for poly( $\beta$ -L-aspartate)s with medium

size side groups. In all cases the helices are right-handed and the chains are arranged in anti-parallel. A second crystal form was found for the ethyl, propyl and n-butyl derivatives. This is a tetragonal structure which consists of a parallel arrangement of 4/1-helices. In spite of the structural variability with the size of the side group, a feature general to the whole family of these polyamides can be concluded from this work. Thus, it may be stated that all the helical structures of poly( $\beta$ -L-aspartate)s are composed of right-handed helices stabilised by intramolecular hydrogen bonds.

### References

- [1] Fernandez-Santin, J.M.; Aymami, J.; Rodriguez-Galan, A.; Munoz-Guerra, S.; Subirana, J.A. *Nature* (London) 1984, **311**, 53.
- [2] Fraser, R.D.B.; MacRae, T.P. in "Conformation in Fibrous Proteins", Academic Press, New York, 1973.

### X-Ray Diffraction From Branched Polyethylenes: Evidence for a Partially Ordered Component

A.M.E.Baker and A.H.Windle

Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge, CB2 3QZ.

We have examined fifteen samples of commercial branched polyethylenes by powder and fibre diffraction. The fibre diffraction was recorded from a novel fibre diffractometer based on a scanning CCD camera, recently designed and built in our department [1]. The diffraction patterns were fitted using the CCP13 suite of programs for the fibre data and the Rietveld method for the powder data. Fitting to the whole pattern was dominated by the two intense lowest angle reflections, (110) and (200) and produced a poor fit to the higher angle reflections. Separating each pattern into a low angle region containing (100) and (200) and a high angle region containing all other reflections produced good fits; however, cell parameters from these were incompatible. The (110) and (200) reflections consistently occurred at lower angles than expected from the higher angle reflections. This discrepancy between the observed and calculated positions increased with higher levels of branching.

Polymers are traditionally viewed in terms of a crystalline and a non-crystalline component. It is