

Fiber I Synthetic Polymers

MS13.01.01 NEW ROUTES TO THE STRUCTURE OF DISORDERED POLYMERS THROUGH COUPLED SCATTERING AND MODELLING. GR Mitchell, Polymer Science Centre, JJ Thomson, Physical Laboratory, University of Reading Whiteknights Reading RG6 6AF UK

The local structure of disordered polymers remains a challenging area of polymer science. The interactions between chain segments lie at the heart of many central issues including miscibility in blends, crystallisation of non-periodic chains and in deformation processes. Although simulation procedures such as molecular dynamics are powerful tools, their complete reliance on the correctness of the force-fields employed limits their usefulness in many cases. We have developed atomistic molecular modelling tools which allow the tremendous level of information in a neutron or x-ray scattering pattern to be exploited directly in the model construction. The particular utility of broad Q neutron scattering with an extended Q range and the possibility of isotopic substitution will be highlighted. These tools are essentially Monte Carlo procedures in which the fit between calculated and experimental structure factors play the same role as the energy of the system in a conventional simulation. A particular feature of these procedures is the manner in which the chemical connectivity is directly involved. Examples demonstrating the power of these new procedures will be given. We have been able to extract the level of orientational segmental correlations has been obtained from experimental data alone for a series of polymers with differing degrees of backbone flexibility. The possibility of linking these procedures with energy based methods will be discussed.

MS13.01.02 THE CRYSTALLIZATION OF APERIODIC POLYMER CHAINS. Alan Windle, Department of Materials Science and Metallurgy, Pembroke Street, Cambridge, UK CB2 3QZ

Polymers with aperiodic chains have a quite remarkable ability to crystallise. However, there are a number of distinctly different mechanisms which enable a chemically aperiodic chain to contribute to the three dimensional periodicity of a crystal lattice.

The paper will review several different systems as examples of mechanistic types, and in each case explore the diffraction consequences. The systems described will be: polyvinyl alcohol, polyvinyl chloride, branched polyethylene, PET/PEN random copolymers, and thermotropic random copolyesters. The issues addressed will include sequence rejection, defect inclusion, conformational adjustment and sequence matching in the crystalline phases.

MS13.01.03 X-RAY FIBRE DIFFRACTION STUDIES OF STRUCTURAL VARIATION IN POLYMER MATERIALS. Watson Fuller, Physics Department, Keele University, Staffordshire, ST5 5BG, UK

Recent developments at the European Synchrotron Radiation Facility (ESRF) and the Daresbury Laboratory Synchrotron Radiation Source (SRS) have allowed a dramatic extension of the structural information which can be obtained in fibre diffraction studies of polymer materials. Three types of application will be described. These are: (i) The exploitation of the high brilliance of the two sources to record diffraction patterns with exposure times as short as 40 milliseconds with the facility for real time display of the accumulating pattern. A Photonics Science CCD detector linked to a Synoptic i860 framegrabber is used to record the pattern and a purpose designed camera allows the development of orientation and crystallinity in polymer materials to be investigated under con-

ditions comparable to those of industrial processing, i.e. draw rates up to 150,000% min, draw ratios up to 4.5 and temperatures up to 350°C. This x-ray camera has a video port which allows changes in the gross appearance of a specimen and hence the draw rate and draw ratio at the point in the specimen from which x-ray data is observed to be continuously recorded and displayed during the experiment. (ii) Beamline ID13 at the ESRF with focusing optics which provide an incident beam at the specimen with a diameter of ~ 2 microns has been used with an X/Z stepping stage to investigate the variation in crystallinity and orientation in spherulites of organic polymers and across polymer interfaces and artefacts fabricated from polymer materials. (iii) Beamline 16.1 at the SRS has been developed to allow the simultaneous recording of the variation in small angle x-ray scattering (SAXS) and wide angle x-ray scattering (WAXS) during drawing and annealing of a number of organic polymers, thus allowing the development of lamellae to be correlated with changes in polymer chain conformation and packing.

MS13.01.04 ON THE STRUCTURE OF A NEW NYLON: POLY(2-METHYLPENTAMETHYLENE TEREPHTHALAMIDE). François Brisse, Annie Héroux, Département de chimie, Université de Montréal, CP 6128, Succursale Centre-ville, Montréal H3C 3J7, Quebec, Canada

The title aliphatic-aromatic polyamide (2M5T nylon) is related to the nT nylons having an odd number, n = 3, 5, 7, of methylene groups. The X-ray diffraction patterns of these polyamides have a very poor resolution. However, that of poly(2methyl pentamethylene terephthalamide) is very well resolved and yields thirty distinct diffraction spots to a d_{\min} of 2.12 Å. The unit cell dimensions, obtained by a trial and error method using all the observed reflections, are: a = 4.96, b = 28.35, c = 26.82 Å (fiber repeat), and $\gamma = 88.3^\circ$. The density measurement reveals the existence of twelve chemical units per unit cell but since the fiber repeat, p = c, indicates the presence of two chemical units in the c dimension, there are six polyamide chains per unit cell. The value of the fiber repeat precludes a fully trans conformation. The structure of the polymer chain was investigated by conformational analysis and the study of model compounds. The diffracted intensities were used to select and confirm the model most likely to represent the structure of the polyamide.

Since the fiber repeat of both the 5T and the 2M5T nylons are nearly identical, it is expected that they adopt the same conformation. That the two nylons have very similar diffraction patterns further confirms the above statement.

MS13.01.05 NEUTRON STRUCTURE ANALYSIS OF POLY(VINYL ALCOHOL). Yasuhiro Takahashi, Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan.

Two crystal structure models were proposed by Bunn and Sakurada et al., which were different in the azimuthal angle of the molecular plane and the hydrogen bonding network. In neutron diffraction, hydrogen atom contributes to the intensity more than X-ray diffraction. Therefore, it is possible to determine the azimuthal angle more accurately and to clarify the position of the hydrogen atom associated with the hydrogen bond. Commercially supplied poly(vinyl alcohol) fiber was used for the sample.

Neutron diffraction experiments were made at JAERI. The intensity distributions on the equator were measured at 100K, 200K, and room temperature. The integrated intensity was estimated after the indices were assigned. The refinements were carried out under the rigid-body assumption. Here, the hydrogen atoms associated with the hydrogen bonds were not incorporated, since the hydrogen atom positions cannot be assumed because of the statistical distribution of the oxygen atoms due to the atactic configuration. The refinements by using the data at 100K, 200K, and room temperature gave R-factors, 26.8, 24.8 and 20.3 %, respectively. The

structures obtained are essentially the same as Bunn's model. The molecule slightly rotates as the temperature increases. The discrepancy factors are not so good. This may be attributed to the fact that the hydrogen atoms associated with hydrogen bonds were ignored. Therefore, the difference synthesis was made by using the data at 100K. It is possible to find three peaks on the map of the difference synthesis. Two peaks can be interpreted by the intermolecular hydrogen bonds as Bunn suggested. Third peak should be attributed to the intramolecular hydrogen bonds in the isotactic sequence of the atactic configuration, which was first proposed by Murahashi et al. for the isotactic poly(vinyl alcohol).

MS13.01.06 STRUCTURAL STUDIES ON NYLONS WITH MORE THAN ONE DIRECTION OF HYDROGEN BONDS.

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Although nylons have been known for well over 60 years, there still remains considerable confusion in the literature concerning the nature and stability of their crystalline structures. However all the stable structures reported at low temperature have a single hydrogen bond direction as a common characteristic. More confusing is the nature of the pseudo-hexagonal structures attained when nylons are heated above the "Brill transition temperature" and also the metastable pseudo-hexagonal structures characteristic of quenched samples. Whereas earlier models postulated random amide rotational jumps of 60° to explain the high temperature hexagonal phases (Brill, *Prakt. Chem.* 161, 49, 1942), the later experimental evidences suggest transitions involving methylene segment librations (Wendolowski et al, *Science* 247, 431 1990).

In recent years, we have carried out a systematic effort aimed at investigating polyamides in which an isolated methylene group is placed between two amide groups. Although a pseudo-hexagonal packing is characteristic, the experimental data point to structures with either three (Belle et al, *Polymer* 35, 1231, 1994), two (Aceituno et al, *Macromolecules* in press) or one (Franco et al, *Macromolecules* 27, 4284, 1994) hydrogen bond direction(s) which are different from the conventional γ form of nylons. Crystallographic and quantum mechanical studies on model compounds support these new structures and also reveal that some dicarboxylic units as glutaryl residues (Navarro et al, *J. Am. Chem. Soc.* 117, 7307, 1995), tend to be in a folded conformation, where the two C-O directions are rotated. With these results on hand we study the nylons 65 and 55 as representatives of glutaric acid derivatives. Experimental data from uniaxially oriented fibers and lamellar crystals show a monoclinic or a pseudo-hexagonal unit cell, depending on the diamine unit. However the results suggest similar structures where each molecule is linked to its four neighbors by a network of hydrogen bonds made by amide groups in two different orientations. Particular conformations for the glutaryl residues play a decisive role in establishing such a unique structure. Temperature-induced structural changes have also been studied, showing that the monoclinic packing of nylon 65 reverts to a pseudo-hexagonal one at 190° C. Modifications are believed to occur without changes in the hydrogen bond system.

MS13.01.07 X-RAY ANALYSIS OF THE SELF ASSEMBLING TUBULAR STRUCTURES FORMED BY POLYMETHACRYLATES WITH HIGHLY TAPERED SIDE GROUPS J. Blackwell, S.N Chvalun, Y.K. Kwon and V. Percec, Department of Macromolecular Science, Case Western Reserve University, Cleveland OH 44106-7202, USA

A poly(methacrylate) with highly tapered side chains: poly{2-[2-(2-methacryloyloxyethoxy)ethoxy]ethoxy}ethyl-3,4,5-tris(p-dodecyloxy-benzyloxy)-benzoate}, has been shown to form an ordered hexagonal structure at room temperature, and to undergo transitions to a columnar hexagonal liquid crystalline phase above ~40°C and to an isotropic phase above ~100°C. In the columnar hexagonal phase, the structure consists of cylinders of diameter 60.4Å at 40°C, decreasing to 53.0Å at 95°C, in which there is little internal order other than limited stacking correlations for the side chains. In the ordered hexagonal state at room temperature, the cylinders have an ordered internal structure with an axial repeat of 5.03Å. Based on the observed density, this repeat would contain 8 monomer units within a cylinder of diameter 59.8Å (at 21.6°C). Strong off-meridional intensity on the first layer line suggests that the "planes" of the aromatic units are tilted by 40-50° to the chain axis. Possible 8-fold helical models have been refined to obtain qualitative agreement with the observed X-ray intensity data. Parallel investigations of the structure of the unpolymerized monomer precursor also show the existence of supramolecular assemblies forming ordered hexagonal and columnar hexagonal phases. Of particular interest are the dimensional changes that occur with temperature, and the effect of annealing on these data.

PS13.01.08 DIFFRACTION STUDIES OF POLYSILANES AND POLYSILAETHYLENES. B. L. Farmer, D. B. Holt and E. K. Karikari*, Dept. of Materials Science and Engineering, University of Virginia, and L. V. Interrante, Dept. of Chemistry, Rensselaer Polytechnic Institute; *Present address: High Performance Polymers and Ceramics Center, Clark Atlanta University

Poly(di-n-alkyl silanes), having the formula $-(SiR_2)-$, display both an ordered structure (the exact nature of which depends on the specific alkyl group) and a disordered structure, described as hexagonal packing of rod-like molecules. Polysilaethylenes, having the general formula $-(SiR_2-CH_2)-$, also undergo a transition to a disordered phase prior to melting. Diffraction studies are being used to characterize the ordered structures and the nature of the disordered phases for these series of materials.

Poly(di-n-pentyl silane) [PdnPS] has a 7/3 helical conformation in the ordered phase at room temperature. A planar zig-zag conformation has also been observed in a sample of PdnPS cooled to -15°C for several hours. The diffraction pattern is consistent with a unit cell having dimensions $a=13.7\text{\AA}$, $b=21.4\text{\AA}$, $c=4.0\text{\AA}$, and angles of 90 deg. A transformation to the 7/3 helical structure occurs at 35°C, and the structure disorders at about 70°C. In the disordered phase, neither lateral registry between chains nor a specific helical structure remains.

There are considerable similarities in the powder patterns for the unsubstituted (R=H) and for the symmetrically substituted polysilaethylenes having ethyl, propyl, butyl, or pentyl side chains. Unlike the highly ordered poly(di-n-hexyl silane), only amorphous scattering has been obtained thus far from the poly(di-n-hexyl-silaethylene). The fiber pattern of $-(SiH_2CH_2)-$ indicates that the polymer adopts a planar zig-zag conformation and a unit cell having dimensions $a=5.70\text{\AA}$, $b=8.75\text{\AA}$, $c=3.25\text{\AA}$ and $\gamma=97.6$ deg. In parallel with efforts to obtain fiber patterns, analysis of the powder patterns of the other polysilaethylenes is currently underway, assisted by various modeling techniques.