

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  $\gamma$  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.