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COMPUTER SIMULATION OF ROTATOR PHASES IN LIQUID-CRYSTALLINE POLYMERS

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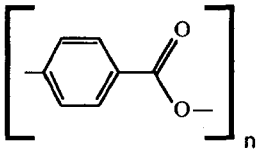
Abstract The high temperature behaviour of the main-chain liquid-crystal polymer poly(hydroxy-benzoic acid) (PHBA) is examined through the use of computer models. PHBA is known to undergo a first order phase transition, at 340°C, from two co-existing orthorhombic crystalline phases to a single pseudohexagonal rotator phase. Although several attempts have been made to establish the nature of this rotator phase, its structure is, as yet, poorly understood. Monte Carlo simulations have been performed on idealised rotator phase models, using energy terms and cell parameters derived from PHBA. Electron diffraction patterns have been simulated, allowing the phase behaviour to be followed. A loss of angular correlations between adjacent molecules is found, which coincides with the crystal-rotator phase transition. The simulated rotator phase structure is compared with previous models which were derived from diffraction data on the basis of symmetry arguments. A possible explanation is proposed for the continued existance of two orthorhombic phases on cooling from the rotator phase.

INTRODUCTION

Polymeric rotator phases are mesophases in which the polymer chains are arranged on a 2-dimensional lattice, but which possess some degree of dynamic rotational disorder about the polymer axis. They are sometimes referred to as highly ordered smectic phases[1], condis crystals[2] or plastic crystals[1]. Rotator phases are common in main-chain liquid crystal polymers, and may play a part in limiting their mechanical properties, especially at elevated temperatures.[3,4]

The aim of the current work is to study the rotator phase found in one particular liquid crystal polymer at high temperatures. The material under examination is the aromatic polyester, poly(para-hydroxy-benzoic acid) (PHBA):



The PHBA monomer forms an important component of several commercial main-chain liquid-crystalline polymers.[4,5] At room temperature, PHBA forms two orthorhombic crystalline phases, phases I and II.[6] Phase I is more abundant in polymeric samples,

whereas phase II is more common in oligomers. However, samples usually contain a mixture of both. Structural models for phases I and II have recently been proposed.[7] On heating, both orthorhombic phases undergo a first order phase transition, at around 340°C, forming what appears from electron diffraction and n.m.r. measurements to be a pseudohexagonal rotator phase (phase III).[6,8] Several attempts have been made to establish the nature of this rotator phase,[9-12] but some features still remain unclear. The current view is that phase III resembles a highly ordered smectic E phase, in which the layers are a single monomer thick, and the polymer chains are perpendicular to the layers. Further heating produces another phase (phase IV) at around 440°C, in which the diffraction pattern appears to be truly hexagonal. This phase has some similarity to a smectic B phase.[10,11]

As mentioned above, phases I and II both transform to phase III on heating, with phases I and II re-forming in the same proportions on cooling.[6,13] However, more recent results suggest that, in fact, phase I can be transformed into phase II, by annealing the polymer in phase III, close to the transition temperature to phase IV.[7] The coexistance of phases I and II is not yet understood.

In order to gain an insight into the structures of PHBA at elevated temperatures, we have performed Monte Carlo simulations on idealised rotator phase models. In this paper, we examine the changes in symmetry of the model as the temperature is increased and the different phases are explored. The results will be compared with previous models for PHBA which were derived on the basis of diffraction data alone. We also propose a possible explanation for the coexistance of phases I and II.

THE COMPUTER MODEL

A two dimensional computer model was constructed in order to simulate a single layer of monomers in the PHBA crystal. This is shown in Figure 1a, where the phenyl rings in one layer are edge-on in a typical herringbone arrangement. The lattice parameters were determined from X-ray diffraction data,[9] and extrapolated to the higher temperatures simulated. The thermal expansion is mainly in the *a* direction, with the ratio of *a:b* being

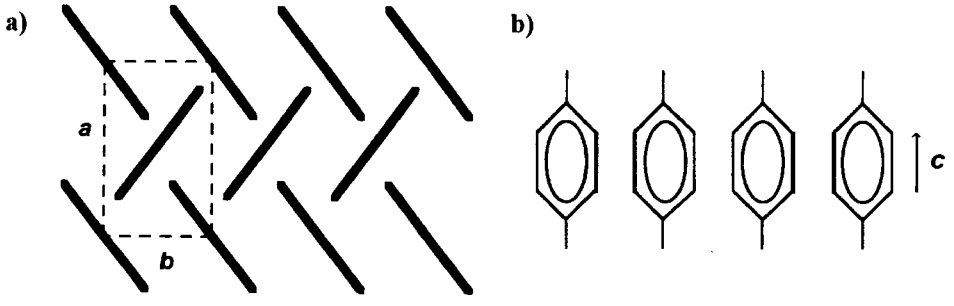


FIGURE 1 (a) A single layer of monomer units, as viewed down the *c* axis of the polymer. (b) The same layer viewed from the side.

slightly less than $\sqrt{3}$ in phase III and equal to $\sqrt{3}$ in phase IV. For simplicity, the ester groups were ignored. The model thus consisted of an array of rotating phenyl groups (Figure 1b). Interaction energies were determined using the Dreiding force field.[14]

Each model consisted of an array of 25 by 25 unit cells, *i.e.* 2500 monomers in total. A Metropolis Monte Carlo algorithm was used to sample the NVT ensemble by making random rotations of the phenyl groups. Each system was equilibrated for 4000 Monte Carlo steps, after which data were collected for a further 400 Monte Carlo steps. Electron diffraction patterns were calculated, showing the a^*-b^* net, in order to determine the symmetry and phase of the system. Angular correlation functions were also evaluated.

RESULTS

Simulations were performed between -10°C and 825°C (Figures 2 and 3). The first point to note about the diffraction patterns is that the underlying orthorhombic lattice appears as a rectangular array of sharp diffraction spots in all cases. However, the more interesting features of these patterns are the diffuse regions of diffraction, observed between the spots, which give information about the level of orientational disorder.

At -10°C (b = 5.7Å, a:b = 1.30, phase I), the monomers form an almost perfect herringbone array, with one or two lattice defects running vertically through the structure. However, when the temperature is increased to 353°C (b = 5.4Å, a:b = 1.70, phase III), additional peaks are observed in the centre of each reciprocal lattice cell, corresponding to new herringbone structures forming at ~60° to the original. Vertical diffuse streaks are also observed, linking the new reflections. Thus, as expected, this pseudohexagonal phase does not possess hexagonal symmetry.[9-11]

The simulated diffraction pattern becomes hexagonal when the temperature is increased to 525°C (b = 5.5Å, b:a = $\sqrt{3}$, phase IV). The hexagonal symmetry arises from the superposition of three herringbone structures, 60° apart, although the short range order makes this difficult to see in the figure. It is clear though that, the underlying structure cannot be truly hexagonal unless all chains become equivalent. In practise, this will only occur at much higher temperatures, when there is sufficient free volume for the chains to become uncorrelated.

To explore this possibility, we performed additional simulations at 675 and 825 °C (see Figure 3), using extrapolated values for the unit cell parameters. At 675°C (b = 5.8Å, b:a = $\sqrt{3}$) the underlying lattice now appears hexagonal, but there is still diffuse scattering between the reciprocal lattice points, suggesting that there is still some short range correlation between the orientations of adjacent molecules. At 825°C (6.6Å, b:a = $\sqrt{3}$) the correlations are finally lost.

Finally, we examined the size of the orientational correlations within our models, as a function of temperature. As expected, a large drop in the magnitude of the correlations occurs at around 345°C, which corresponds to the first order transition between phase I and phase III.

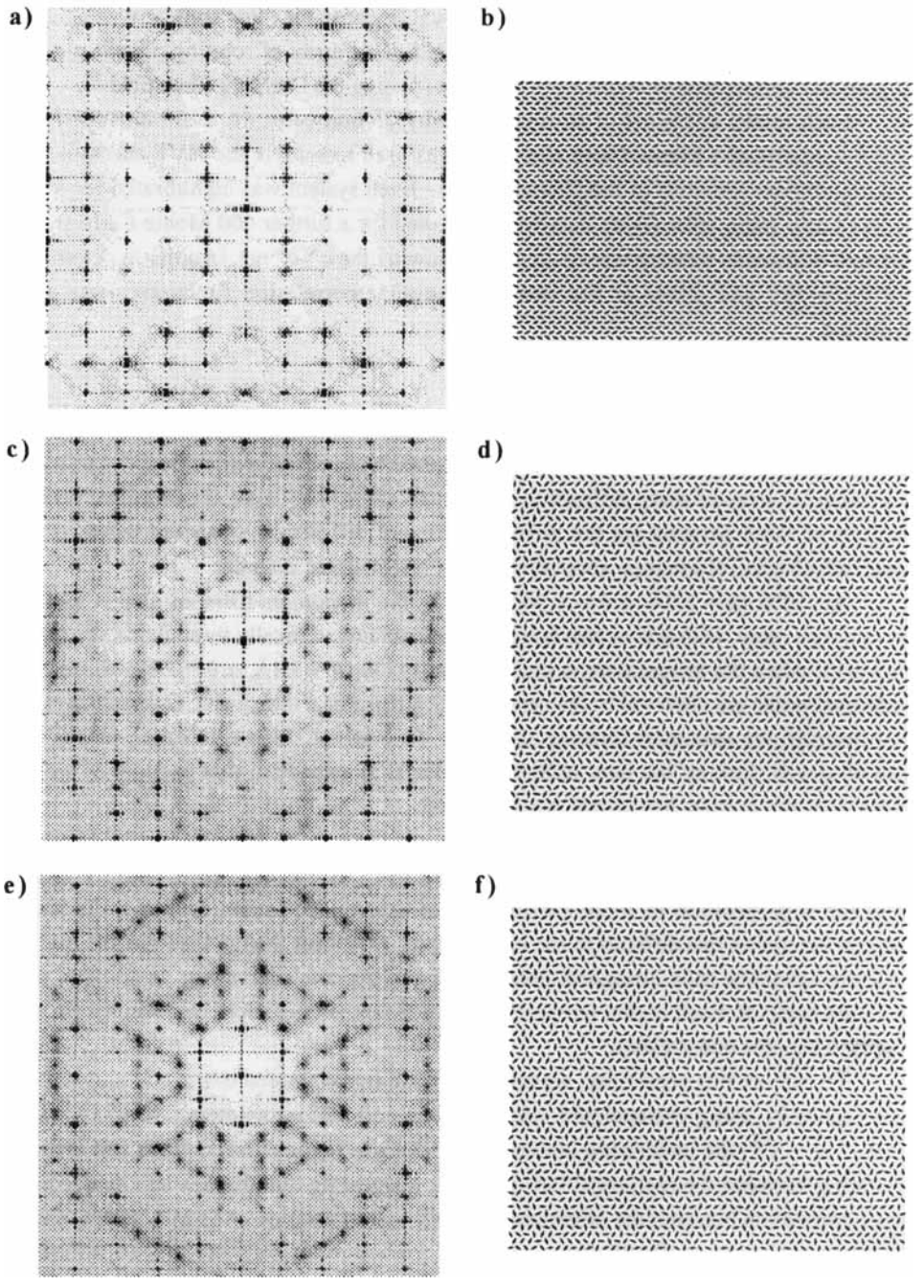


FIGURE 2 Electron diffraction patterns (a^*-b^* net) and sample configurations at -10°C (a,b), 353°C (c,d) and 525°C (e,f). The plots are all oriented so that b or b^* are horizontal. The reciprocal space axes run from -5.5 to +5.5 $Å^{-1}$ with the origin at the centre of the plot.

DISCUSSION

The simulations show a phase transition and formation of a pseudohexagonal phase at around 345°C, in agreement with the X-ray diffraction results. There is a corresponding loss of long-range orientational order, but short-range order is still present, indicating that any rotational motion which occurs must be cooperative. Indeed, it is striking that orientational correlations, albeit very short-range, persist for several hundred degrees above the rotator phase transition temperature, making it clear that free rotation will never occur in the real polymer. Our results are in line with previous models for phases III and IV, which describe them as smectic E and B respectively.

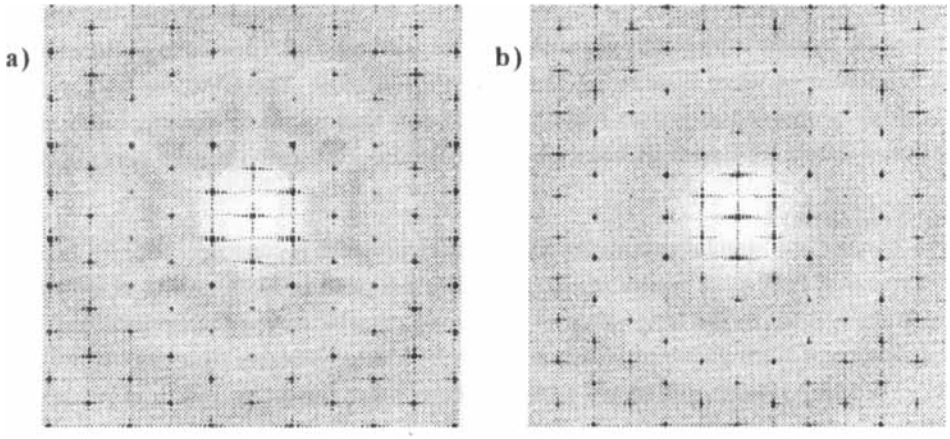


FIGURE 3 Electron diffraction simulations at (a) 675°C and (b) 825°C. The scale and orientation is the same as Figure 2.

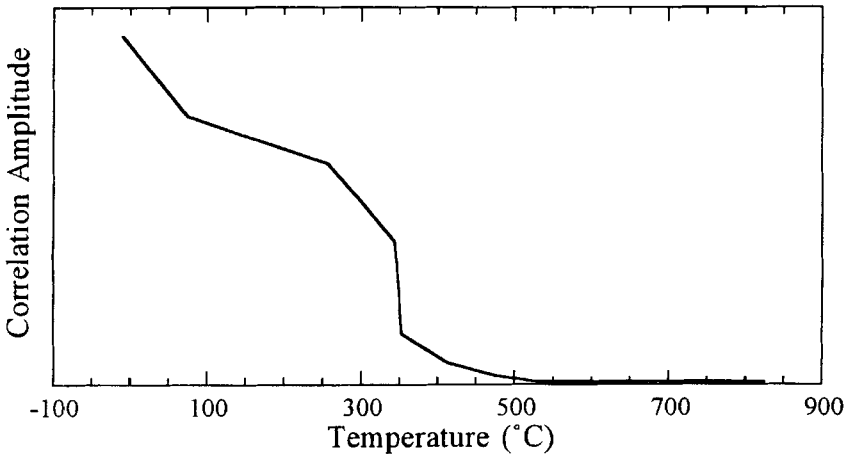


FIGURE 4 Graph showing size of angular correlations between monomer units as a function of temperature.

Although, in principle, it is possible to form a herringbone structure in three different orientations at elevated temperatures, it is clear that the shape of the lattice prevents the three orientations from occuring in equal proportion, unless $a = \sqrt{3}b$. This raises an interesting point, regarding the relative orientations of phase I and phase III. If, in phase III, there is a preference for the herringbone orientation which corresponds to the phase I structure, this implies that phase III has a memory of the phase I orientation. We might speculate, that a similar effect could occur for the transformation from phase II to phase III. If we consider the structures of phases I and II,[7] and extrapolate them both to 353°C, we find that the principal differences are in the setting angles of the polymer chains. Therefore, to transform between these two phase III structures would require considerable reorientation of the chains, which our results suggest is unlikely to happen, unless the system is heated to phase IV. In fact, Iannelli and Yoon have demonstrated such a transition when close to the phase III / IV boundary. Therefore, we suggest that the exact proportion of phases I and II in PHBA is determined by kinetic, rather than thermodynamic consideration, caused by the constraints on rotation present in phase III.

CONCLUSIONS

The Monte Carlo simulations predict phase behaviour which is consistent with the known behaviour of PHBA. A rotator phase (phase III) is formed at 345°C, which is indicated by a sharp drop in the long-range orientational correlations in the system, and the appearance of herringbone structures at 60° to the low temperature structure. However, the diffraction pattern still shows a clear orthorhombic symmetry. Only in phase IV, when $a = \sqrt{3}b$, do the three possible herringbone orientations occur in equal proportions. The lattice distortion present in phase III may be sufficient to prevent the transformation between nascent regions of phase I and phase II material. At the highest temperatures experimentally accessible, the diffraction patterns possess six-fold symmetry. However, locally, the structure still resembles a herringbone structure, with short range order.

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