Structure and temperature-induced structural changes of various polyamides

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The structure and temperature-induced structural changes of three polyamides, PA 6, PA 6.6 and PA 6.10, were investigated by X-ray diffraction. In all three polyamides a reduction of the distance in the hydrogen-bonded sheets was measured. A discontinuity in the temperature dependence of the *d*-spacings d_{100} and $d_{110+010}$ was found only in PA 6.10 and 6.6. This can be interpreted by a change of the arrangement of the hydrogen bonds. Because of the existence of two equatorial peaks up to the melting point in PA 6 and PA 6.10, a non-statistic distribution of the hydrogen bonds can be assumed. In PA 6 the planar arrangement of the hydrogen bonds is maintained.

(Keywords: polyamide; structure; polymorphism)

Introduction

Polyamide (PA) can be synthesized by condensation of (1) aminoacids (PA 6) or (2) diamines and dibasic acids (PA 6.6 and PA 6.10). An important difference in the chemical structure is the number of the amino carbon groups per chemical repeat unit, which is one for PA 6 and two for PA 6.6 and PA 6.10:

$\text{+(CH}_2)_5\text{–NH–CO+}_n$ PA6

$\text{+(CH}_2)_6\text{–NH–CO–(CH}_2)_4\text{–CO–NH+}_n$ PA6.6

$\text{+(CH}_2)_6\text{–NH–CO–(CH}_2)_8\text{–CO–NH+}_n$ PA6.10

PA can exist in different crystalline structures. The highest ordered modification is the so-called α-form. This α form is described by a monoclinic (PA 6) or triclinic (PA 6.6 and 6.10) unit cell with hydrogen bonds arranged nearly in the [1 0 0] direction, when [0 0 1] is parallel to the chain axis. The α form develops preferentially at high crystallization temperatures or low cooling rates from the molten state. At rather low crystallization temperatures or rather high cooling rates the material crystallizes in the pseudohexagonal γ structure, especially in PA 6[1]. Because of its molecular structure and its fast and perfect crystallization, PA 6.6 cannot easily be transformed into a γ-like structure. Nevertheless, this structure, or a poorly ordered α structure, is observable at certain temperatures during crystallization from the glassy state[2]. The γ structure is unstable and can be transformed into the α structure by thermal treatment[3–7]. *Figure 1* shows the wide-angle X-ray scattering (WAXS) patterns of amorphous and semicrystalline PA 6, containing γ and α structure.

It has been found by Brill[8] that the two strongest interferences of the α form in the WAXS diagram, the 2 0 0 and 0 2 0+2 2 0 interferences (in PA 6.6 and PA 6.10 these are the 1 0 0 and 0 1 0+1 1 0 interferences), become closer with increasing temperature. In PA 6.6 these two interferences apparently merge into one. The position of the 2 0 0 interference (1 0 0 interference) is nearly constant[8] or even changes to a higher diffraction angle[9,10], which means a contraction in the corresponding lattice direction. The 0 2 0+2 2 0 interference (0 1 0+1 1 0 interference) shifts, as expected, to a lower diffraction angle with increasing temperature. Possible reasons for the different thermal behaviour of the crystalline phase in the individual directions are the anisotropy of the thermal expansion[11], the development of a three-dimensional network of hydrogen bonds due to rotational vibrations of the macromolecules[8,12,13], or a non-first-order phase transition to a new crystalline phase or unit cell[14].

Because of the uncertainty in the interpretation of WAXS diagrams, further measurements on highly crystalline PA, combined with profile fitting as an evaluation method, were carried out to help to elucidate the dependence of the structure of the α phase on temperature.

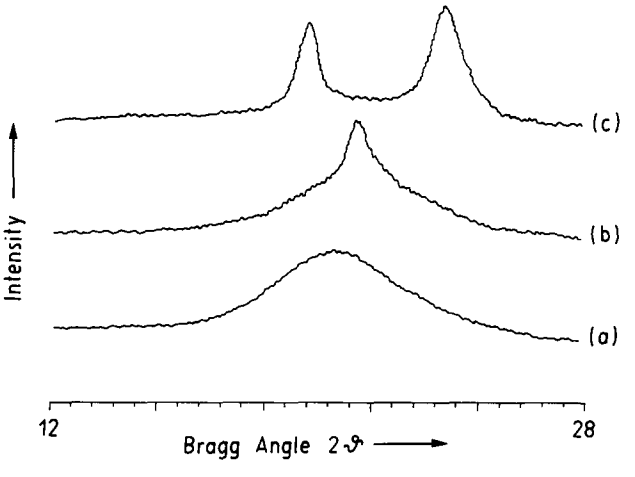

Figure 1 WAXS diagrams of amorphous (a) and semicrystalline PA 6 containing (b) γ and (c) α structure

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Experimental

X-ray diffraction was applied in order to investigate the temperature dependence of the supermolecular structure of various polyamides (commercial products from BASF, Germany). An URD 63 diffractometer (Präzisionsmechanik Freiberg GmbH, Germany) was used. The $I(2\vartheta)$ diagrams were registered in dependence on temperature by using a temperature chamber (A. Paar KG, Austria). The chamber was evacuated in order to minimize thermal degradation. The heating rate was $2\ \mathrm{K\ min^{-1}}$. A position-sensitive detector was applied to measure a high number of $I(2\vartheta)$ diagrams in dependence on temperature ($\Delta T \simeq 7$ K) with minimal angle increment ($\Delta 2\vartheta = 0.02°$) and a maximum counting time ($\Delta t = 22$ s). Although the peaks of interest are relatively close together, the diagram was measured in a wider range ($2\vartheta = 10$–$30°$) in order to have a profound basis for fitting the profile. Therefore a module of the APX 63 program (Präzisionsmechanik Freiberg GmbH, Germany) was used. As an example, *Figure 2* shows the separated profile of PA 6, which contains the α, γ and amorphous δ-phase. The input of the start values for the fit is simple for the crystalline interferences. The justification for input of the start values of the amorphous halo was the $I(2\vartheta)$ diagram of the completely amorphous PA, which was prepared by quenching (see *Figure 1a*)[2]. For measurement of the temperature dependence of the structure of the α phase, samples with high crystallinity were used. In the case of PA 6 and PA 6.6, such specimens were prepared by crystallization from solution with HCOOH at 293 K.

Results and discussion

Figures 3–5 show the X-ray diagrams of the investigated

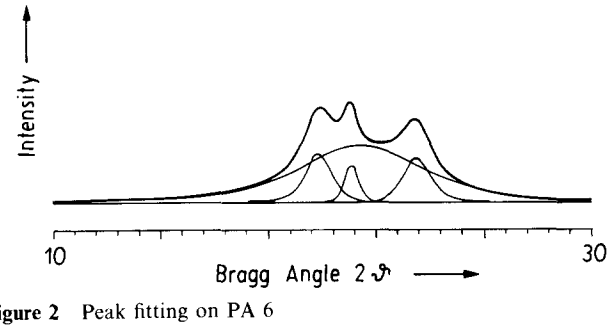

Figure 2 Peak fitting on PA 6

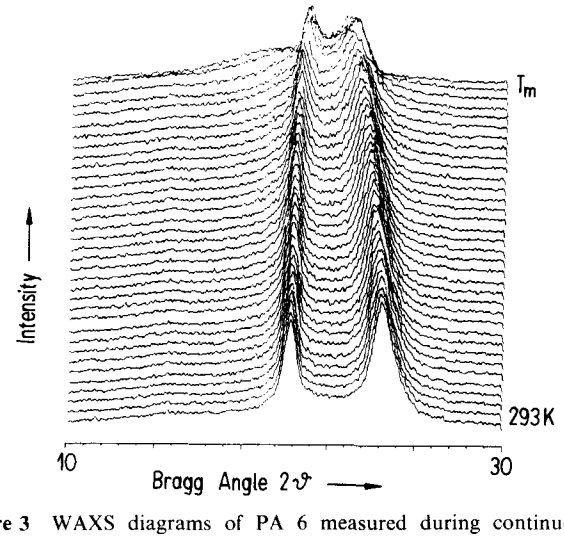

Figure 3 WAXS diagrams of PA 6 measured during continuous heating

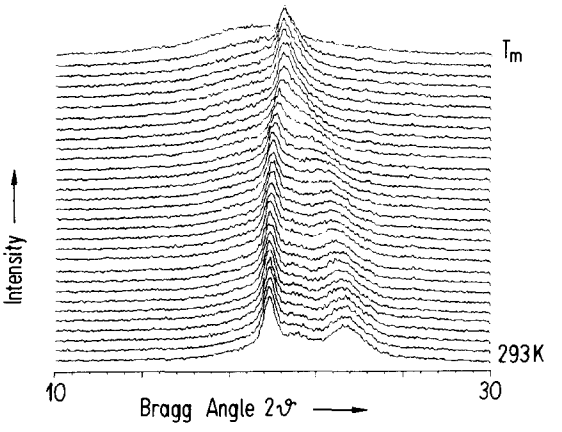

Figure 4 WAXS diagrams of PA 6.10 measured during continuous heating

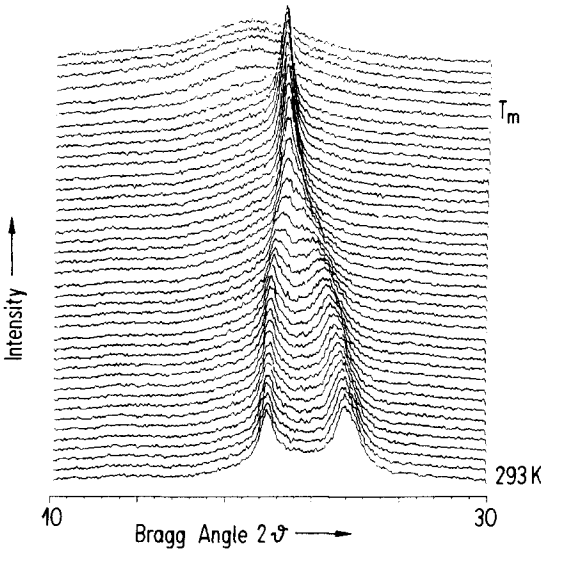

Figure 5 WAXS diagrams of PA 6.6 measured during continuous heating

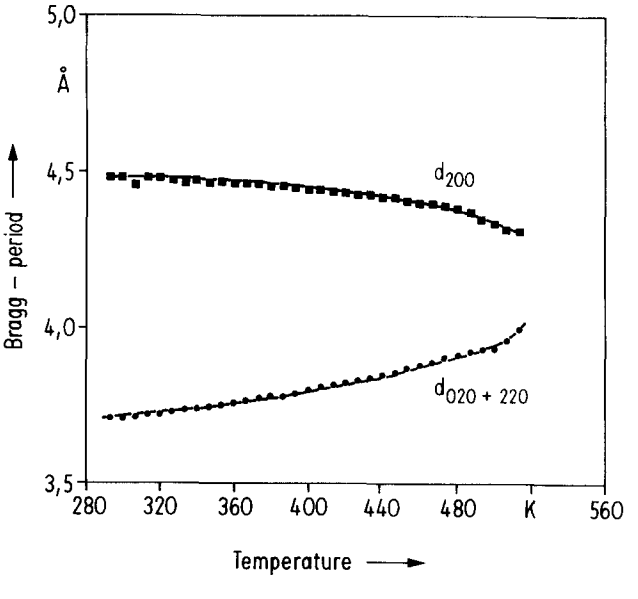

Figure 6 Dependence of d-spacings of PA 6 on temperature

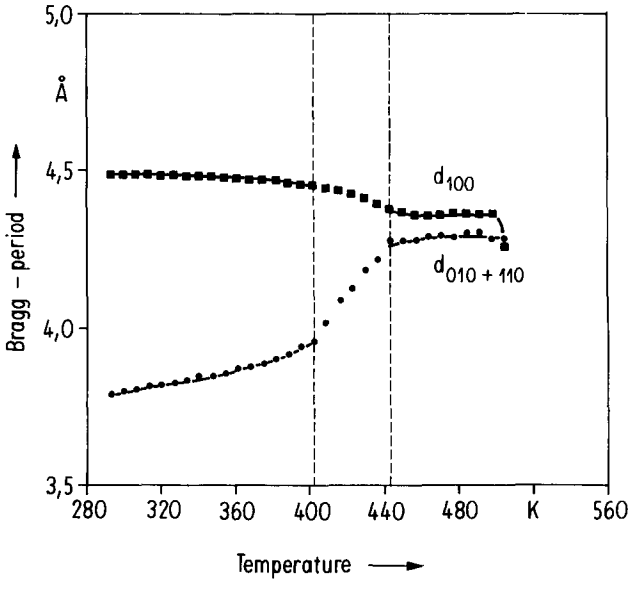

Figure 7 Dependence of d-spacings of PA 6.10 on temperature

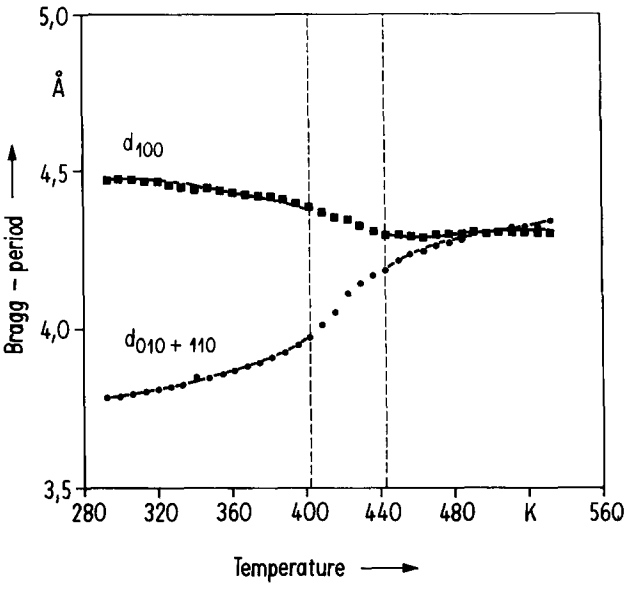

Figure 8 Dependence of d-spacings of PA 6.6 on temperature

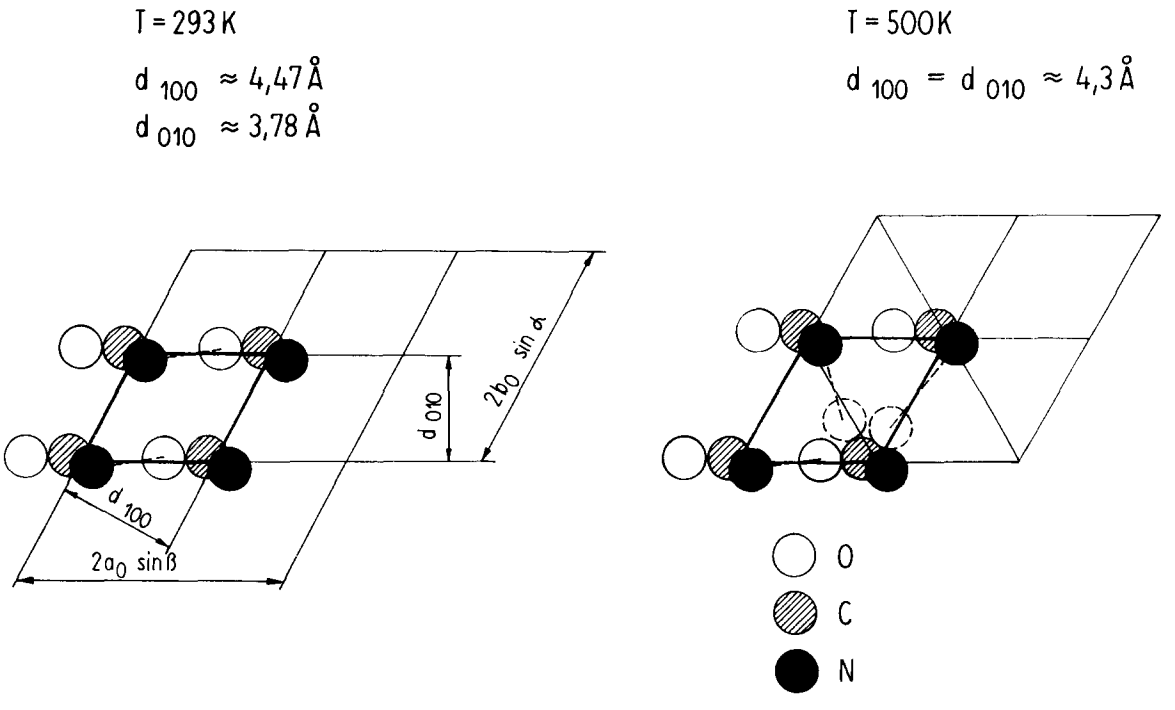

Figure 9 Projection of the basal plane of the unit cell of PA 6.6 at room temperature and 500 K

polyamides, measured during continuous heating. In all three samples a shift of the 200 peak (100 peak) to a higher diffraction angle is visible, which means a shortening of the distance of the hydrogen bonds. While there is complete merging of the two equatorial peaks into one peak in PA 6.6, the peaks are separated up to the melting point in PA 6 and 6.10. The plot of the intermolecular spacings d_{220} (d_{110}) (*Figures 6–8*), after fitting of the measured profile in dependence on temperature, reveals the characteristic differences in the thermal behaviour of PA 6, 6.6 and 6.10.

In PA 6, over the whole temperature range between room temperature and the melting temperature, there is a continuous change of the d-spacings. In contrast to PA 6, there is an over-proportional change of the d-spacings or even a discontinuity in the diagram of d_{220} (d_{110} in the case of PA 6.6 and PA 6.10) *versus* temperature at about 400 K in PA 6.6 as well as in PA 6.10. This discontinuity could indicate the development of a three-dimensional network of hydrogen bonds, as suggested by Brill[8] or Schmidt[13]. While in PA 6.10 the two peaks are visible in the original diagram, and also the two d-spacings after fitting up to the melting point, both peaks seem to merge completely in PA 6.6. This would imply a pseudohexagonal unit cell in the PA 6.6 α crystalline phase, whereas the unit cell remains monoclinic or triclinic at high temperatures in PA 6 and PA 6.10. But the fitting procedure also shows the existence of two different interplanar specings in the cross-chain direction of PA 6.6. It is possible to calculate such a

behaviour on the foundation of the measured values, but it is not visible in the original diagram.

Because there is no qualitative change in the thermal behaviour in PA 6, the result of the measurement (*Figure 6*) can be explained by normal anisotropic thermal expansion. The reason for the reduction in the distance towards the hydrogen bond is that the chain requires less space in this direction with increasing temperature owing to vibrations of the molecule[12]. It can be supposed that the planar arrangement (on average) of the hydrogen bonds is maintained, which is not so in PA 6.6 and PA 6.10. Without further proof, a connection to the chemical structure can be assumed, but further experiments on other polyamides are necessary. The discontinuity in these two polyamides at about 400 K can be interpreted by a partial breaking of the hydrogen bonds and a rotation towards the [1 1 0] or [0 1 0] direction owing to an increased torsion of the chain with increasing temperature. *Figure 9* shows the projection of the basal plane based on our measurement of the interplanar spacings of PA 6.6 at room temperature and at 500 K. Such a folding-down of hydrogen bonds and the building-up of a new bond to a neighbouring sheet, i.e. in a different lattice direction as in PA 6.6, is not possible in PA 6 because of staggering of the neighbouring sheets by a distance of 3/14 c. This is why in PA 6 no hydrogen bonding is possible in the [1 1 0] or [0 1 0] direction without changing the overall crystalline structure.

Conclusions

X-ray diffraction experiments in dependence on temperature, in connection with a comprehensive evaluation by using a computer program for fitting the measured profile, have shown differences in the thermal behaviour of the polyamides PA 6, PA 6.6 and PA 6.10. In crystalline PA 6, the *d*-spacings in the cross-chain direction are changing continuously, whereas in PA 6.6 and PA 6.10 there is a discontinuity during heating. The observed reduction of the distance d_{100} *or* d_{200}, which is in the direction of the hydrogen bonds, can be explained by thermal vibrations without breaking the hydrogen bonds. The discontinuity in the thermal dependence of the *d*-spacings in PA 6.10 and PA 6.6 is due to partial breaking and rotation of hydrogen bonds.

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