Calorimetric, X-Ray and Infra-Red Investigations on Poly(hexamethylene adipamide)

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Summary In dependence on crystallization conditions three ranges with different crystal structure and heat of fusion were found by DSC, WAXS, and IR for unoriented PA 6.6 samples of densities between 1.10 and 1.17 g cm⁻³:

- Range I: α_I triclinic, ρ_c=1.225 g cm⁻³, ΔH_c=235 J g⁻¹.
- Range II: α_{II} triclinic, ρ_c=1.165 g cm⁻³, ΔH_c=185 J g⁻¹.
- Range III: Continuous variation from ρ_c, ΔH_c to ρ_{II}, ΔH_{II}. ρ_a=1.095 g cm⁻³ is independent of crystallization conditions. The transition between α_I and α_{II} is probably due to changes of the chain conformation.

Introduction For many polymers a linear relationship exists between the X-ray crystallinity w_c (or the experimental heat of fusion ΔH*) and the specific volume v. Earlier measurements (1,2) revealed an unusual behaviour of polyamide 6.6 (PA 6.6) which has now been investigated by different experimental methods.

Experimental PA 6.6 samples of crystallinities between 0.05<w_c<0.65 were crystallized from the melt, the glassy state and dilute solutions by varying the crystallization time t_c and the crystallization temperature T_c. ΔH* was measured by a DuPont-Thermal-Analyzer (DSC). The complete premelting is included into the determination of the peak area. Transmission wide angle X-ray measurements (WAXS) were performed by means of a Philips diffractometer and the X-ray
crystallinity calculated from the integrated amorphous and crystalline intensities $F_a$ and $F_c$ of randomly oriented samples by $w_c = F_c / (F_c + \alpha F_a)$ (3,4). After subtraction of the amorphous halo the crystalline scattering is decomposed into the (002), (100), and (010)/(110) peaks using a DuPont-Curve-Resolver in order to determine the accurate angular positions of these peaks. The infra-red (IR) spectra of PA 6.6, measured by a Perkin-Elmer-Model 325, were decomposed by computer analysis. The decomposition is necessary for correct determinations of wave numbers and intensities. In this way new absorptions were detected (598, 660, 714, 922 and 938 cm$^{-1}$). The densities of the samples were measured by the floating method at 20 °C using $\text{CCl}_4\text{-n-heptane}$ mixtures. All measurements were performed with carefully dried samples.

Results and discussion In Fig.1 $w_c$, the intensity $F/d$ of the "crystalline" IR absorption at 936 cm$^{-1}$, and $\Delta H^*$ are plotted versus specific volume $v$. Each of the three experimental methods obviously reveals the same kind of anomaly. The experimental results are arranged upon two straight lines I and II which are connected by a transition along curve III.

Range I represents PA 6.6 samples, which were crystallized from the melt at $T_c > 220$ °C, from the glass at $T_c > 200$ °C or from dilute solution. Crystallization from the glass at $T_c < 100$ °C and from the melt for $t_c < 30$ s at $T_c < 220$ °C is represented by range II. All the other crystallization conditions produce samples within the transition range III. By extrapolation to zero crystallinity ($w_c = F/d = \Delta H^* = 0$) $v_a = 0.913 \pm 0.002 \text{cm}^3\text{g}^{-1}$ is obtained for the specific volume of amorphous PA66 from each of the three experimental methods. This value is much lower than the hitherto accepted value of 0.935 cm$^3\text{g}^{-1}$ (5).