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

H. Haberkorn, K. H. Illers and P. Simak

Meß- und Prüflaboratorium, BASF Aktiengesellschaft, 6700 Ludwigshafen am Rhein, Federal Republic of Germany

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 gcm^{-3}: Range I: α_I triclinic, $\rho_c^I=1.225$ gcm^{-3}, $\Delta H_M^I = 235$ Jg^{-1}. Range II: α_{II} triclinic, $\rho_c^{II}=1.165$ gcm^{-3}, $\Delta H_M^{II}=185$ Jg^{-1}. Range III: Continuous variation from ρ_c^I, ΔH_M^I to ρ_c^{II}, ΔH_M^{II}. $\rho_a=1.095$ gcm^{-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 be means of a Philips diffractometer and the X-ray

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crystallinity calculated from the integrated amorphous and crystalline intensities F_a and F_c of randomly oriented samples by $w_c=F_c/(F_c+\varkappa F_a)$(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 CCl_4-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 ΔH^* 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 ($w_c=F/d=\Delta H^*=0$) $v_a=0.913\pm0.002 cm^3g^{-1}$ 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^3g^{-1} (5).

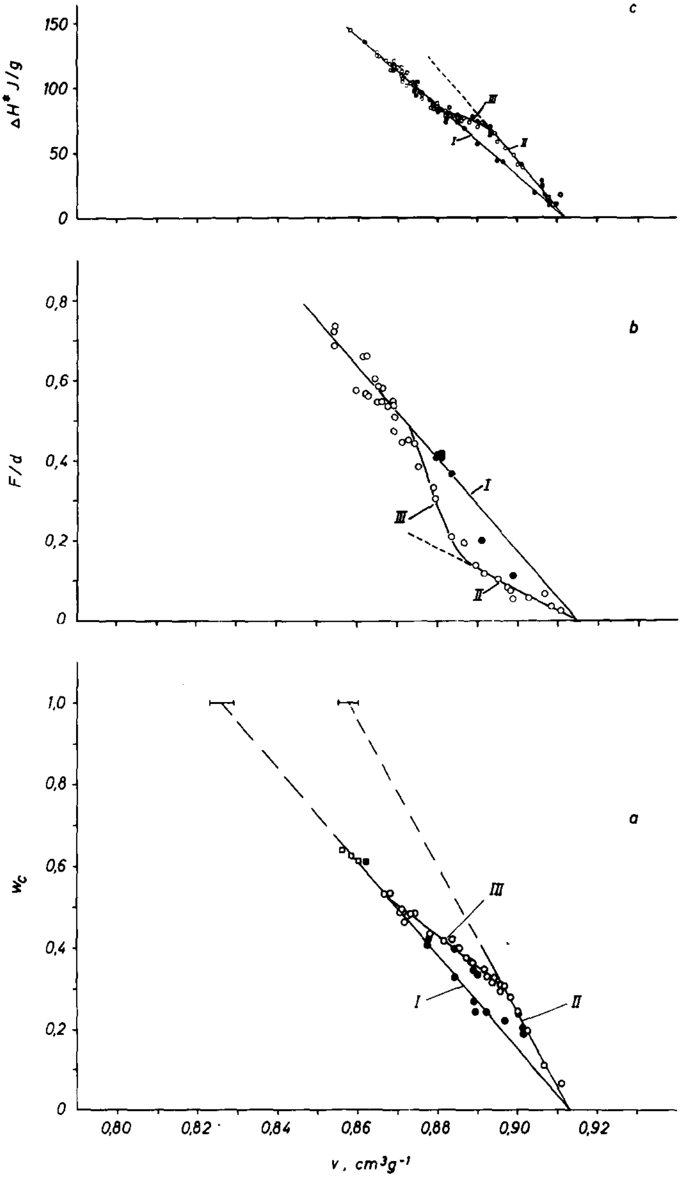

Fig.1: X-ray crystallinity w_c, IR intensity F/d of the 936 cm^{-1} absorption, and experimental heat of fusion ΔH^* of PA 6.6 versus specific volume v at 20 °C.

○ from glassy state
● from melt
■ from dilute solution
□ in superheated H_2O (180°C)

By extrapolation of line I in Fig.1a to $w_c=1$ the specific volume of the triclinic α_I-crystal is found to be $v_c^I=0.826\pm0.003$ cm^3g^{-1}.If the intensity of the"amorphous" 1148 cm^{-1} absorption, plotted versus v, is extrapolated to F/d=0, the same v_c is obtained, which nearly agrees with (5). The corresponding crystal density $\rho_c^I=1.210\pm0.005$ gcm^{-3} is much lower than the commonly accepted $\rho_c=1.24$ gcm^{-3} (6). This discrepancy partly results from the fact, that our samples of range I contain small amounts of α_{II}-crystals (see below), which have grown during quenching from T_c.If this fraction of α_{II}-crystals is taken into account (7), $\rho_c^I=1.222$ gcm^{-3} is obtained, which agrees with the crystal density $\rho_c^I=1.225$ gcm^{-3} determined from the mean square electron density fluctuation (7),but still is lower than the value in (6).The remaining difference is not due to a lower order in our α_I samples (Fig.2).

The linear extrapolation of line II in Fig.1a up to $w_c=1$ leads to the specific volume $v_c^{II}=0.858\pm0.003cm^3g^{-1}$ of the α_{II}-crystal ($\rho_c^{II}=1.165\pm0.005$ gcm^{-3}).

The angular positions 2θ of the (100) and (010)/(110) WAXS peaks and the angular difference Δ2θ,the changes of which are thought to reflect changes in lateral order, are plotted versus v in Fig.2a and 2b.Also these two plots clearly show the regions I, II, and III. Similar changes in the angular positions of these WAXS peaks were reported at rising temperatures (8), which recently were related to variations of the chain conformation (9). The angular position of the (002) peak, which represents the longitudinal (c-axis) order, exhibits similar variations (Fig.2c).

The main conclusions drawn from Fig.2 are the following:
i) The α_{II} crystal is triclinic,too,with lateral order corresponding to $\Delta 2\theta\approx0.8$ degr. and longitudinal order corresponding to $2\theta_{(002)}\approx12.8$ degr.

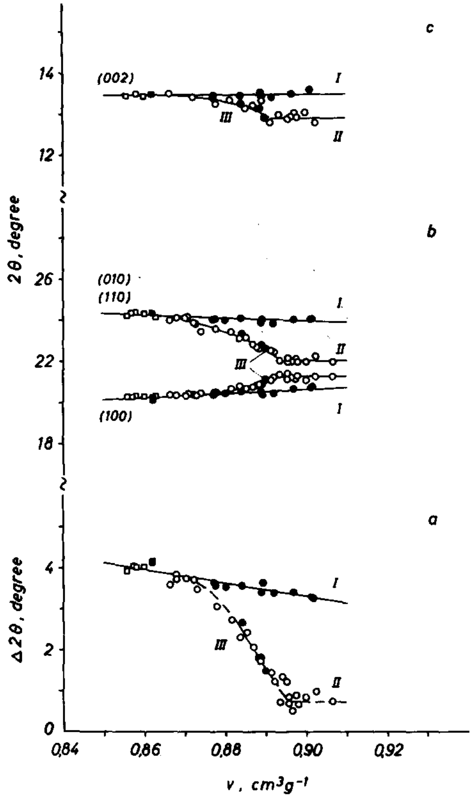

Fig.2: Angular positions of the WAXS peaks of PA 6.6 versus v at 20 °C. For symbols see Fig.1.

ii) The transition within region III is probably accompanied by a continuously varying chain conformation which is also to be seen in the behaviour of the 938 cm^{-1} IR absorption (7).

The heats of fusion of the α_I and α_{II} crystal are $\Delta H_M^I=235\ Jg^{-1}$ and $\Delta H_M^{II}=185\ Jg^{-1}$ (7). The crystallinity of randomly oriented PA 6.6 samples can be determined by WAXS in an unequivocal and reproducible manner regardless of v, whereas the calculation of crystallinity from v or ΔH^* is only possible if the samples belong to range I or II. Samples belonging to range III undergo a continuous variation of ρ_c and ΔH_M with crystallization conditions. The varying ρ_c^{III} can be determined from the mean square electron density fluctuation (7). The calculation of ρ_c^{III} from unit cell parameters (10,11) is only a very rough approximation, because the constancy of the b- and c-axis lenght and of the triclinic angles α, β, γ, assumed for the calculations, is not fulfilled, as is to be concluded from Fig.2.

A detailed description and discussion of the presented results will be published elsewhere (7).

References

(1) ILLERS, K.H. and HABERKORN, H.: Makromol. Chem. 146, 267 (1971)

(2) ILLERS, K.H.: Progr. Colloid & Polymer Sci., 58, 61 (1975)

(3) HERMANS, P.H. and WEIDINGER, A.: Makromol. Chem. 44-46, 24 (1961)

(4) HENDUS, H. and SCHNELL, G.: Kunststoffe, 51, 69 (1961)

(5) STARKWEATHER JR., H.W. and MOYNIHAN, R.E.: J. Polymer Sci., 22, 363 (1956)

(6) BUNN, C.W. and GARNER, E.V.: Proc. Roy. Soc. (London), 189A, 39 (1947)

(7) HABERKORN, H., ILLERS, K.H. and SIMAK, P.: Colloid & Polymer Sci., in press

(8) STARKWEATHER JR., H.W., WHITNEY, J.F. and JOHNSON, D.R.: J. Polymer Sci., A 1, 715 (1963)

(9) COLCLOUGH, M.L. and BAKER, R.: J. Mat. Sci., 13, 2531 (1978)

(10) HINRICHSEN, G.: Colloid & Polymer Sci., 250, 1162 (1972)

(11) GURATO, G., ARNAVAS, A., CANAL, P. and ZANNETTI, R.: Makromol. Chem., 180, 537 (1979)

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