Polymer Bulletin 6, 559–564 (1982)

Polymer Bulletin

Raman Spectrum of the High Pressure Phase of Polyethylene

R. Eckel[1], H. Schwickert[1], M. Buback[2] and G.R. Strobl[1]

[1] Institut für Physikalische Chemie der Universität Mainz, D-6500 Mainz, Federal Republic of Germany

[2] Institut für Physikalische Chemie der Universität Göttingen, D-3400 Göttingen, Federal Republic of Germany

Summary

The Raman spectrum of the hexagonal high pressure phase of polyethylene was measured at 5.2 kbar and 240 °C, using a hydrostatic high pressure cell. The spectrum is largely identical to that obtained for the melt. This result indicates that the conformational short range order in the hexagonal phase remains melt - like and is not modified by the overall straightening of chains.

Introduction

For pressures above 3.5 kbar a new phase appears in PE. This high pressure phase lies intermediate between the orthorhombic crystalline phase and the melt (BASSETT & TURNER 1972). Its special importance arises from its responsibility for the formation of the "chain - extended" morphology, which is known to develop in samples crystallized under high pressure (WUNDERLICH & ARAKAWA 1964). BASSETT (1976) demonstrated that the extended chain lamellae, which have thicknesses of several thousand Angströms, are the result of nucleation and growth in this high pressure phase. Thermodynamic and structural properties of this phase were investigated in a number of studies. According to calorimetric and dilatometric measurements transitions in and out of the high pressure phase are of first order, the much larger changes in enthalpy and volume occurring with the transformation into the orthorhombic phase (BASSETT & TURNER 1972, LEUTE & DOLLHOPF 1980). The X-ray scattering pattern is indicative

0170-0839/82/0006/0559/$01.20

for a hexagonal packing of chains with a very low degree of intramolecular order (BASSETT, BLOCK & PIERMARINI 1974; YAMAMOTO 1979). Compared to the orthorhombic phase there is an increase in the cross - section area per chain by 13 % accompanied by a shrinkage along the chain by 5 %. Obviously the conformation is different from a regular all - trans form. Two microscopic structure models were put forward so far. PECHOLD et al. (1976) suggest a perturbed helix, YAMAMOTO (1979) proposes a locally perturbed all - trans chain.

Experimental

In this communication we report the Raman spectrum of the high pressure phase. It was obtained with a newly constructed high pressure Raman cell which can be used up to 7 kbar and 300 °C. The sample was surrounded by silicone oil and put under hydrostatic pressure. Pressures were generated with a cylinder - piston system and measured with a precision of ±10 bar. The sample compartment was closed by a steel bellow. The bellow - expansion or - contraction was monitored using an inductive device which enables a detection of changes in sample volume. A detailed description of the cell is given elsewhere (ECKEL, BUBACK & STROBL 1981). Experiments were performed on a fractionated linear polyethylene ($M_n = 1.0 \cdot 10^5$, $M_w/M_n = 7.5 \pm 2$) supplied by the Hoechst AG.

Results and discussion

The registration of the motion of the steel bellow in the cell permits a clear detection of the transitions and phases passed during increasing the pressure on the sample starting from the melt. These observations were supported by a measurement of the intensity and polarization of the laser beam after passage through the sample. A two - step decrease in the transmitted intensity (melt: I_0 → hexagonal phase: $0.25 \cdot I_0$ → orthorhombic phase: $0.03 \cdot I_0$) and a simultaneous increase in the depolarisation ratio (melt: $I_\perp / I_\parallel = 0$ → hexagonal phase: $I_\perp / I_\parallel = 0.9$

→ orthorhombic phase: $I_{\perp}/I_{\parallel} = 1$) was registered just at the pressures where the volume changed.

Figs. 1, 2 and 3 show in a comparison Raman spectra obtained for the melt at 240 °C and 4 kbar pressure near to the phase transition, the hexagonal phase at 240 °C and 5.2 kbar, the orthorhombic phase just after the transformation (240 °C, 5.9 kbar) and under normal conditions. The spectra refer to three conformationally sensitive regions:
the CH_2 - bending range (fig. 1), the CH_2 - twisting range (fig. 2) and the CC - stretching range (fig. 3) (TASUMI & SHIMANOUCHI 1965).

The main result is clear: the Raman spectra of the hexagonal phase are nearly identical to those of the melt. There are no detectable differences with the exception of a minor change in the CC - stretching range. Generally the Raman scattering pattern of disordered chains is built up of a variety of bands associated with different vibrations of

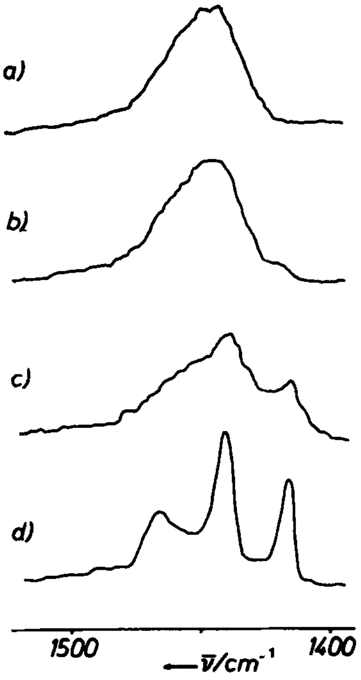

fig. 1. Raman spectra of HDPE
CH_2 - bending range .
a) melt
(240 °C, 4.0 kbar)
b) hexagonal phase
(240 °C, 5.2 kbar)
c) orthorhombic phase
(240 °C, 5.9 kbar)
d) orthorhombic phase
(RT, 0 kbar)

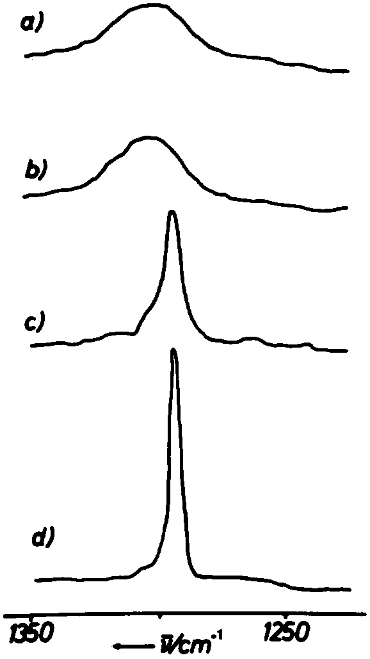

fig. 2: Raman spectra of HDPE CH_2 - twisting range

a) melt
(240 °C, 4.0 kbar)
b) hexagonal phase
(240 °C, 5.2 kbar)
c) orthorhombic phase
(240 °C, 5.9 kbar)
d) orthorhombic phase
(RT, 0 kbar)

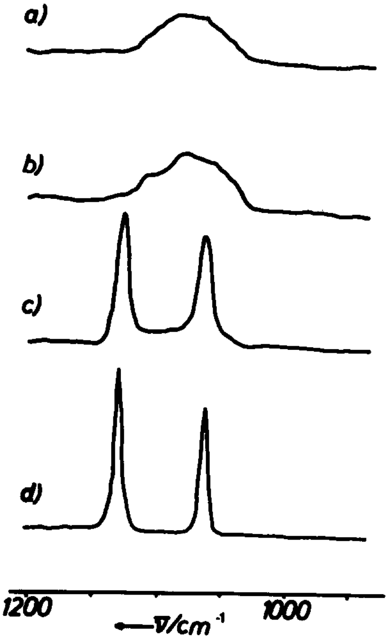

fig. 3: Raman spectra of HDPE CC - stretching range

a) melt
(240 °C, 4.0 kbar)
b) hexagonal phase
(240 °C, 5.2 kbar)
c) orthorhombic phase
(240 °C, 5.9 kbar)
d) orthorhombic phase
(RT, 0 kbar)

local character which involve only a few structure units and depend upon their respective rotational isomeric states. Therefore, Raman spectra can be considered as being related to and reflecting the conformational short range order along the chain. Our result indicates that the transition from the melt to the hexagonal phase leaves this short range conformational distribution unchanged. On the other hand, long range order is imposed in the hexagonal phase. Here chains can only realize all those conformations which fit into a tube with cross section area 20.6 Å. Our result suggests that this long range order is introduced without a substantial change in the short sequence conformer distribution. This conclusion is supported by the comparatively small values measured for the enthalpy and volume increases at the transition to the melt. Both quantities are also related to the conformational short range order. Hence, all observations so far speak in favour of a chain conformation in the hexagonal phase,which is melt - like for short sequences, although a long range order exists.

The spectra observed for the orthorhombic crystalline phase are dominated by the all - trans bands. No amorphous contributions can be detected in the spectra of the chain - extended samples under normal conditions. High temperature and pressure result in a line - broadening. The majority of chains appears to remain in the all - trans form up to the phase transition.

Acknowledgements

Thanks are due to Prof. Cherdron and Dr. Böhm, Hoechst AG for supplying the sample. The work has been supported by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 41 "Chemie und Physik der Makromoleküle").

Literature

BASSETT, D.C., TURNER, B.; Nature 240, 103 (1972)

BASSETT, D.C., BLOCK, S. PIERMARINI, G.J.; J.Appl.Phys. 45, 1891 (1974)

BASSETT, D.C.; Polymer 17, 460 (1976)

ECKEL, R., BUBACK, M., STROBL, G.R.; Coll.& Pol.Sci. 259, 326 (1981)

LEUTE, U., DOLLHOPF, W.; Coll. & Pol.Sci. 258, 353 (1980)

PECHOLD, W., LISKA, E., GROSSMANN, H.P., HÄGELE, P.C.; Pure a. Appl. Chem. 46, 127 (1976)

TASUMI, M., SHIMANOUCHI, T.; J. Chem. Phys. 43, 1245 (1965)

WUNDERLICH, B., ARAKAWA, T.; J. Polym. Sci. A2, 3697 (1964)

YAMAMOTO, T.; J. Macromol. Sci. -Phys. B16, 487 (1979)

Received February 6, accepted February 8, 1982