

# A RAMAN-SPECTROSCOPIC STUDY OF PHASE STRUCTURE OF DRAWN POLYETHYLENE\*

YAN Rongjiang (闫荣江) AND JIANG Bingzheng (姜炳政)

(Changchun Institute of Applied Chemistry, Academia Sinica, Changchun 130022)

## ABSTRACT

A drawn high density polyethylene (HDPE) has been measured by Raman spectroscopy and differential scanning calorimetry (DSC). The crystalline structure of drawn HDPE is analysed by the Raman internal modes in terms of mass fractions of the crystalline orthorhombic phase, the liquid-like amorphous phase and the disordered anisotropic phase. The mass fractions depend on draw temperature  $T_d$  and draw ratio  $R_d$ . The fraction of disordered anisotropic amorphous phase changes very little with the  $T_d$  and increases with increasing  $R_d$ . Sum of the mass fractions of crystalline orthorhombic phase and the disordered anisotropic phase increases linearly as the same slope as the crystallinity  $W_c$  determined from DSC measurements with increasing  $T_d$  or  $R_d$  and it is higher than the  $W_c$  for all the samples. The results show that the mass fraction of disordered anisotropic phase is partially devoted by the taut tie molecules (TTMs) in the amorphous state. The dependence of the disordered anisotropic phase on  $T_d$  and  $R_d$  supports the mechanism of plastic deformation of fibre structure.

There is a lot of literature regarding the structure of drawn polyethylene (PE)<sup>[1-4]</sup>. One model generally accepted has early been built by Peterlin and his coworkers<sup>[1]</sup>. According to the model, the fibre structure of drawn PE is constituted by microfibrils, in which crystalline and amorphous layers are periodically arranged. Some taut tie molecules (TTMs) exist between and inside the microfibrils, which makes the material have good mechanical quality. Volume fraction of the TTMs in amorphous phase depends on the ratio of elastic modulus of the sample itself to that of its crystalline elements in axis direction,  $E/E_c$ <sup>[4]</sup>. Up to date, there has been no efficient method to exactly characterize the TTMs. The absorbance of infrared band at  $2016\text{ cm}^{-1}$  may be partially devoted by the TTMs<sup>[5]</sup>. Recently, Prasad and Grubb<sup>[6]</sup> studied the peak shift of the Raman band at  $1063\text{ cm}^{-1}$  of a drawn PE fibres and found that the band developed a broad low intensity tail, which is thought to be produced by the interfibrillar TTMs.

Raman spectra of drawn PE have also been used to determine sample's orientation<sup>[7, 8]</sup>, the arrangement of chain segments in crystalline phase<sup>[9]</sup>, and the mechanism of molecule deformation and breaking<sup>[10]</sup>. Strobl and Hegedorn<sup>[11-13]</sup> developed a method to measure the phase fractions of crystalline orthorhombic phase, liquid-like amorphous phase and disordered anisotropic phase for PE samples. The partial melting of low density polyethylene (LDPE)<sup>[11]</sup> and the structure

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of PE crystallized from the melt<sup>[12]</sup> and solution<sup>[13]</sup> were also studied by this method. It should be noticed that Raman spectrum technique offers information on disordered anisotropic phase as well as the broad line  $^1\text{H}$ <sup>[14]</sup> and high resolution  $^{13}\text{C}$ -NMR<sup>[15]</sup>.

In this paper, we have investigated the structure of drawn HDPE by the Raman method together with differential scanning calorimetry (DSC), and discussed the nature of disordered anisotropic phase and the mechanism of plastic deformation.

## EXPERIMENTAL

### *Sample*

Commercial HDPE called Marlex 6001 with  $MFI=0.5$  was produced by the Philips Petroleum Company. The HDPE pellets were pressed in mould for 10 min. at 160 °C, taken in another hydraulic press, and cooled to room temperature. Then about 1 mm thick films were obtained.

The PE film was cut into strips. The strip clamped between two crossheads ( $15 \times 20 \text{ mm}^2$ ) was drawn with a tensile testing machine, INSTRON-1121 after preheated for 10 min. at the predetermined temperature. Draw temperatures are 21, 40, 60, 80, 120 °C respectively. Draw rate was 10 or 20 mm/min. Draw ratio was obtained by pen marks.

It is meaningless to direct analysis the comparative intensity of Raman spectra for drawn samples because of their anisotropic property. In order to guarantee the efficiency of the Raman method, the samples must be macroscopically in random orientation. Therefore, we cut the drawn PE films into so small pellets, which were filled into a glass tube, that many of them arranging randomly could be simultaneously irradiated by the laser beam. The coincidence of the results measured before and after the sample tube was rocked showed that the method was feasible.

### *Raman spectra*

Raman spectra were recorded on the spectrophotometer of model DILOR-Z24. Excitation radiation was 514.5 nm from a Spectra Physics model 165  $\text{Ar}^+$  laser. Scattered light was collected at a right angle with the incident beam. The laser power used was 200 — 300 mW. Slit-width was 400  $\mu\text{m}$  ( $3.3 \text{ cm}^{-1}$ ).

### *DSC*

DSC measurements were performed with a Perkin-Elmer DSC-7 instrument. Sample weight used was 5 — 6 mg, and heat scanning rate 10 °C /min. Percentages of the crystallinity were calculated through the determined fusion heat  $\Delta H_m$  taking the  $\Delta H_m^0$  of pure crystal as 292.6J/g<sup>[16]</sup>.

## RESULTS AND DISCUSSION

The Raman spectra of partially crystallized PE can be regarded as overlapping of the three components, i.e., crystalline orthorhombic phase, liquid-like amorphous phase and disordered anisotropic phase<sup>[11]</sup>. Since the total integrated intensity  $I_T$  of the  $\text{CH}_2$  twisting band at  $1289 \text{ cm}^{-1}$  is irrelevant to the conformations of molecular chains, it may be used as an internal intensity reference. The band at

$1416\text{ cm}^{-1}$  results only from crystalline regions. From the integrated intensity of this band,  $I_{1416}$  the fraction of  $\text{CH}_2$  units in crystalline orthorhombic phase, or crystallinity of the sample was calculated,  $\alpha_c = I_{1416}/0.46I_T$  where the constant 0.46 is measured from the spectrum of fully crystallized PE<sup>[11]</sup>. In  $\text{CH}_2$  twisting vibration region in between ca.  $1330$  and  $1250\text{ cm}^{-1}$ , the half with low wave number of the amorphous band at  $1303\text{ cm}^{-1}$  was principally measured in the experiment data, the other half of the band was deconvoluted by hand, based on that its half-height half-width in high wave number is  $13\text{ cm}^{-1}$  and it has ca. a symmetry width<sup>[11]</sup>. Its intensity  $I_{1303}$  directly reflects amorphous content, i. e.,  $\alpha_a = I_{1303}/I_T$ . Then the fraction of disordered anisotropic phase is given by  $\alpha_b = 1 - \alpha_a - \alpha_c$ . In addition, the amorphous fraction can be also obtained from the band intensity of C-C stretching vibration region. The spectra in this region were not measured since the method has been proved to be efficient for many samples in the published literatures.

Figure 1 presents a collection of characteristic spectra measured in the region  $1230 - 1530\text{ cm}^{-1}$  and indicated analyses for the samples drawn at different temperatures. The  $I_{1416}$  is calculated from half of the band at  $1416\text{ cm}^{-1}$  in lower frequency region. One characteristic in the spectra is that there is a tail in lower frequency region of  $\text{CH}_2$  twisting vibration. Intensity of the tail is not fully

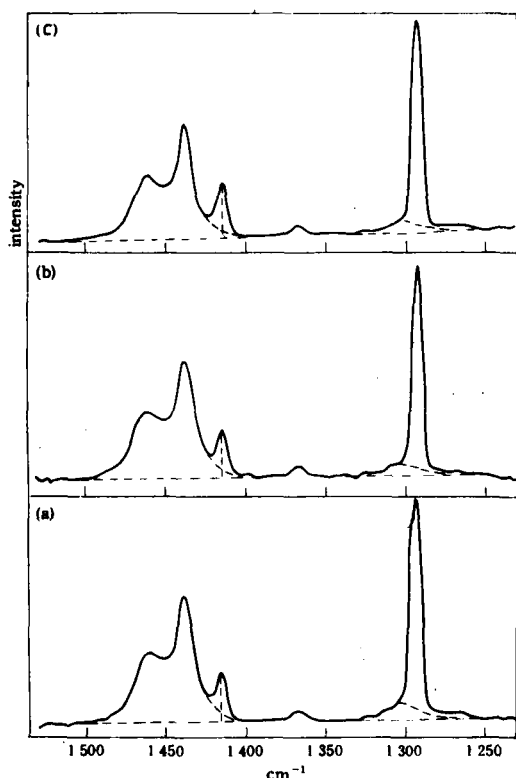


Fig. 1 The typical types of Raman spectra and indicated analyses for the HDPE samples drawn to ratio 7.7 at temperatures :  
(a)  $40\text{ }^{\circ}\text{C}$ , (b)  $80\text{ }^{\circ}\text{C}$ , (c)  $120\text{ }^{\circ}\text{C}$ . Draw rate:  $20\text{ mm/min}$

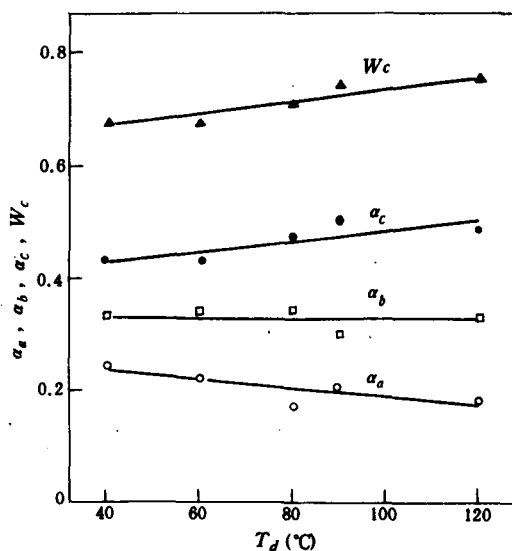


Fig. 2 Plots of the fractions of liquid-like amorphous  $\alpha_a$ , disordered anisotropic phase  $\alpha_b$  and orthorhombic crystalline phase  $\alpha_c$  and DSC crystallinity  $W_c$  as a function of draw temperature. Draw rate:  $20\text{ mm/min}$ . Draw ratio: 7.7

included in the deconvoluted  $1303\text{ cm}^{-1}$  band considering that the band is about symmetrical<sup>[11]</sup>. In Figure 1, no obvious shift of the band positions appears. It can be seen that the intensity of the  $1303\text{ cm}^{-1}$  band decreases while that of the  $1416\text{ cm}^{-1}$  band increases with increasing temperature, indicating that crystallinity of the sample increases but the amorphous content decreases.

Dependence of the three phase fractions from Raman spectra and the crystallinity measured by DSC for the samples drawn to ratio 7.7 on draw temperature is shown in Figure 2. With the increase of temperature, the fraction of liquid-like amorphous phase decreases linearly, and the disordered anisotropic phase has no remarkable change. However, both the fraction of crystalline orthorhombic phase and DSC crystallinity  $W_c$  increase linearly with about the same slope.  $W_c$  is much greater than  $\alpha_c$  for all the samples. It is known that in the HDPE that crystallizes whether from melting state or solution the disordered anisotropic phase fraction is less than 15%<sup>[11-13]</sup>, and lower than that of amorphous phase. This phase has been thought to be the interfacial phase between crystalline and amorphous regions<sup>[12,13]</sup>. However, it is more than 30% for all the samples drawn to ratio 7.7 in Fig. 2. It is unreasonable to fully attribute such a high phase fraction to interfacial phase. In fact, many defects exist in the crystalline region and the amorphous phase is partially ordered in oriented PE sample. The interface is ambiguous and the density difference between crystalline and amorphous phase smaller<sup>[17]</sup>. For highly drawn sample, no obvious two phase structure was observed and the interface became clear only after the sample was annealed<sup>[18]</sup>. On the character of Raman spectra, the intermediate phase stems from extended molecule chains which are laterally disordered. They can be at the interface or in the disturbed region of crystallites (boundaries of mosaic blocks or inner defects)<sup>[11]</sup>. They should also be partially devoted by the TTM's or the oriented molecular chains in amorphous state for drawn samples.

The long period of drawn PE, determined from small angle X-ray scattering (SAXS), is only dependent on draw temperature<sup>[19]</sup>. It is possible that the folded-chain lamella in original sample has transformed to new ones of which the thickness relies on draw temperature. Therefore, crystallinity of the sample increases and the amorphous content decreases with increasing draw temperature (Fig. 2).

DSC crystallinity of unoriented PE is identical with the fraction of orthorhombic crystalline phase  $\alpha_c$ <sup>[12,13]</sup>. However, the DSC crystallinity  $W_c$  of oriented HDPE is evidently higher than the  $\alpha_c$  as shown in Figure 2. This results mainly from the considerable devotion of oriented chains in amorphous phase (or TTM's) to fusion heat<sup>[20-23]</sup>. For instance, fusion heat of amorphous phase takes 40 percent of the total for HDPE sample drawn to ratio 10 at  $60^\circ\text{C}$ <sup>[21]</sup>. If we compare  $W_c$  with the sum  $\alpha_b + \alpha_c$ , we see that the latter has higher value. The fusion heat of PE crystallites is  $271.7 - 309.3\text{ J/g}$ <sup>[16]</sup>. Even if we choose the smallest value  $\Delta H_m^0 = 271.7\text{ J/g}$  to calculate crystallinity  $W_c'$  and compare it with  $\alpha_b + \alpha_c$  as shown in Figure 3, the line of  $\alpha_b + \alpha_c$  is over that of  $W_c'$ . It will be seen from the later discussion that such a difference comes from neglecting the devotion of folded-chain lamella surface to fusion heat. On the other hand, the  $W_c$  and  $\alpha_c$  lines in Figure 2 have the same slope. The correspondence of the two incoherent methods demonstrates indirectly feasibility of Raman spectrum analysis to drawn samples.

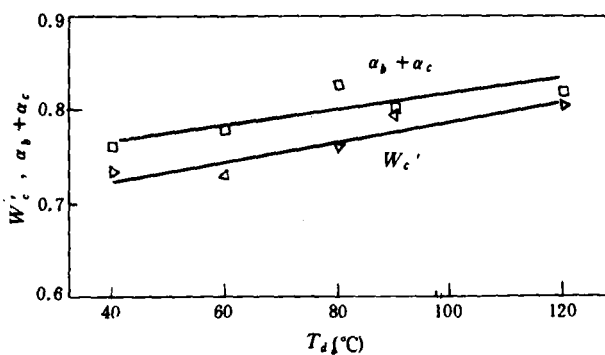


Fig. 3 Dependence of the sum of disordered anisotropic and crystalline phase ( $\alpha_b + \alpha_c$ ) calculated from the data in Figure 2 and DSC crystallinity  $W_c'$  on draw temperature.

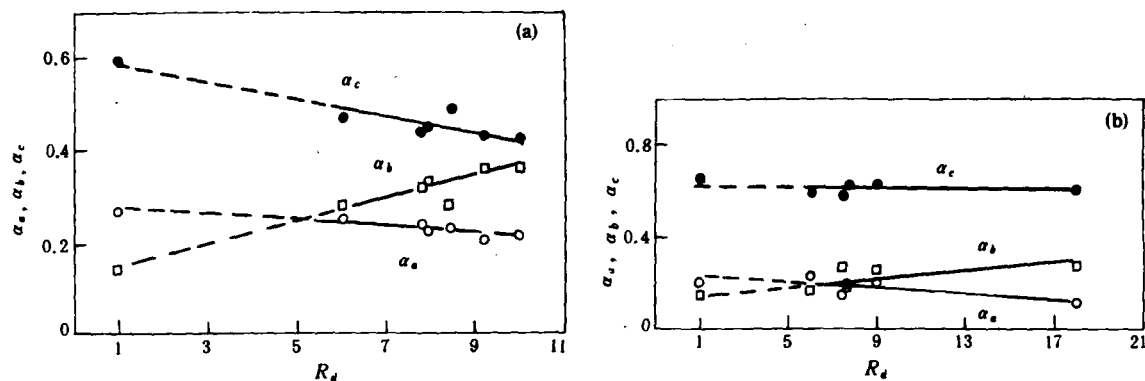


Fig. 4 Schematic representation of the three phase fractions versus draw ratio for the HDPE samples: (a) drawn with a rate of 10mm/min. at 21 °C and (b) drawn with a rate 20mm/min. at 90 °C

Each phase fraction of the samples drawn at 21 °C and 90 °C, calculated by the Raman method, is schematically shown in Figure 4 as a function of draw ratio. For the sample drawn at 21 °C, both crystalline  $\alpha_c$  and amorphous phase fraction  $\alpha_a$  decrease to some extent, but for the samples drawn at 90 °C,  $\alpha_a$  decreases while  $\alpha_c$  changes very little with increasing draw ratio. The disordered anisotropic phase fraction  $\alpha_b$  decreases evidently for both groups of the samples.

After specimen is extended to be necked down, PE spherulitic structure converts into fibril morphology, later the fibrous structure performs plastic deformation<sup>[1]</sup>. All drawn samples in our study (draw ratio,  $R_d > 6$ ) had finished their necking process. Plastic deformation of sample occurs mainly by sliding motion of the fibrils past each other. At the same time, shearing slide of the microfibrils and crystalline chains may happen. These processes make that the TTMs originally relaxed become extended or the TTMs unfold the chain sections where the tie molecules are anchored in the crystalline blocks of adjacent microfibrils. Those all would promote the fraction of efficient TTMs. The shearing slide of crystalline chains may also make a big lamella change into mosaic blocks, or make some folded-chains protrude from crystal regions. Therefore, the fraction

of the disordered anisotropic phase increases, while that of the amorphous decreases (Fig. 4). If the samples were drawn at room temperature, the orthorhombic crystalline phase reduced because the TTMs unfold crystal lamella and the shear slide of crystalline chains makes the lamella more irregular. If the samples were drawn at 90 °C, annealing may lead to some amorphous molecules to crystallize or recover the regularity of crystalline lamella, so the orthorhombic crystalline phase fraction keeps a constant.

Let us compare the crystallinity  $W_c$  with the  $\alpha_b + \alpha_c$  in Figure 5. We find that both of them increase with draw ratio linearly. Either DSC fusion heat or  $\alpha_b + \alpha_c$  determined by Raman spectra is devoted by crystalline, amorphous and interfacial phases, but the devotions of interfacial phase are very different in the two measurements. DSC fusion heat is written as<sup>[20]</sup>:

$$\Delta H_m = \alpha_c \Delta H_m^0 - \alpha_c \Delta H_e + (1 - \alpha_c) \Delta H_n \quad (1)$$

where  $\Delta H_m^0 = 292.6 \text{ J/g}$  and  $\Delta H_n$  are individually fusion heat of crystalline phase and amorphous phase,  $\Delta H_e = 2\sigma/L\rho$  is that of crystal surface,  $\sigma = 7.5 \times 10^{-6} \text{ J}\cdot\text{cm}^{-2}$  is surface Gibbs free energy,  $L$  and  $\rho$  are respectively SAXS long period and density of the sample. Long period of the sample before drawn, measured by SAXS is  $L_0 = 2.57 \times 10^{-8} \text{ m}$ , that of the samples drawn at 21 °C  $L = 2.12 \times 10^{-8} \text{ m}$ . Even if we choose small values,  $L = 2.0 \times 10^{-8} \text{ m}$  and  $\rho = 0.93 \text{ g}\cdot\text{cm}^{-3}$  to calculate out surface energy,  $\Delta H_e = 8.36 \text{ J/g}$ , it is not as much as 3 percent of the total melting heat yet. It is the small devotion of interfacial phase to DSC fusion heat that results in correspondence between the DSC crystallinity and fraction of the orthorhombic crystalline phase for unoriented samples<sup>[12,13]</sup>. Our result (e.g.,  $W_c = 0.64$ ,  $\alpha_c = 0.67$ ) for the undrawn PE is also like this. The  $\alpha_b$  equals to 0.138 and 0.142 for the undrawn sample at 21 °C and 90 °C respectively. These two values are rational to be attributed to the interface fraction. Therefore, the deviation of the results between DSC and Raman spectra in Figures 3 and 5 lies in crystalline interfacial phase, i.e., devotion of the interfacial phase to  $W_c$  can be neglected, but that to the  $(\alpha_b + \alpha_c)$  is quite considerable. On the other hand, the increase of  $W_c$  and  $(\alpha_b + \alpha_c)$  with draw ratio (Fig. 5) results completely from the rising of TTM fraction or dropping of conformation entropy<sup>[22, 23]</sup>.

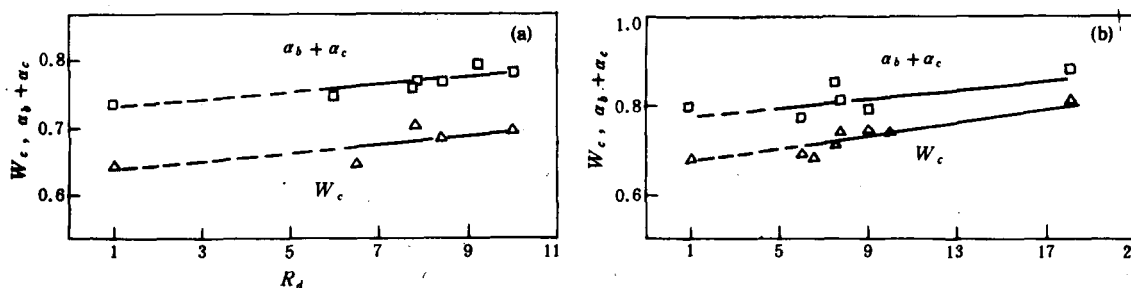


Fig. 5 Dependence of the sum of both the disordered anisotropic phase and the orthorhombic crystalline phase fractions  $\alpha_b + \alpha_c$  and DSC crystallinity  $W_c$  on draw ratio for samples drawn at (a) 21 °C; (b) 90 °C.

The results shown in Figure 4 is seemingly contrary to general consideration that the crystalline phase fraction should increase with increasing draw ratio. In

fact, no available data show exactly that orthorhombic crystalline phase increases as PE is drawn. According to the known data, density of HDPE is raised as it is extended<sup>[23]</sup>. Because the crystallinity determined by density measurements is identical with  $\alpha_b + \alpha_c$  from Raman spectra<sup>[12]</sup>, the increase of density, as well as that of melting point and fusion heat<sup>[21, 24]</sup>, may all result from the TTM's in amorphous phase. Prevorsek and Sharma<sup>[25]</sup> found that drawing of nylon 6 caused a little effect on crystalline size in the direction of orientation, while crystalline width decreased with drawing, which means crystallinity of the sample reduced. The phase structure of extruded PE single fibre drawn at 100 °C has been investigated by wide line NMR<sup>[14]</sup>. When draw ratio of sample rises, the mass fraction of broad component (corresponding to crystalline phase) increases somewhat. The results in Figure 5 are different from this. The difference comes possibly from unequally dividing of phase regions of the samples by the two methods or from the difference of starting samples. The mass fraction of narrow components (corresponding to amorphous phase) decreases, that of medium component increases. Our results from Raman spectra are in accordance with these. In addition, the mass fraction of medium component of sample drawn to 10 times is about 30%<sup>[14]</sup>, and the interfacial phase fraction of PE oriented from gel amounts to 30% measured by high resolution <sup>13</sup>C-NMR<sup>[15]</sup>. Compared with these, the high value of  $\alpha_b$  obtained from Raman spectra is reasonable. The crystallinity of unoriented PE determined by wide angle X-ray diffraction (WAXD) is about equal to the  $\alpha_c$  from Raman spectra<sup>[11]</sup>. Therefore, it is necessary to study the phase structure of drawn PE with WAXD and high resolution <sup>13</sup>C-NMR.

## CONCLUSION

Raman spectra can be used to study the phase structure of drawn PE. The structure of oriented HDPE is divided into orthorhombic crystalline phase, disordered anisotropic phase, and liquid-like amorphous phase. The sum of the orthorhombic crystalline and the disordered anisotropic phase fractions, ( $\alpha_c + \alpha_b$ ) and the DSC crystallinity  $W_c$  increase linearly with the same slopes with increasing draw temperature or draw ratio. For all the samples, the  $W_c$  is higher than  $\alpha_a$ , and lower than the sum, ( $\alpha_c + \alpha_b$ ). It is suggested that both the fusion heat measured from DSC and the disordered anisotropic phase fraction include the devotion of the TTM's in drawn HDPE, but the devotion of the crystalline interface to the former is negligible, to the latter noticeable. On the other side, the fractions of the three phases are dependent on draw temperature and draw ratio, which is in accordance with the mechanism of plastic deformation for crystalline polymers.

### Keywords:

Polyethylene; Raman spectra; Drawing; Crystalline structure; Disordered anisotropic phase.

## REFERENCES

- [1] Peterlin, A., *J. Mater. Sci.*, **1971**, 6, 490.
- [2] Peterlin, A., *Polym. Eng. Sci.*, **1977**, 17 (3), 183.
- [3] Peterlin, A., *Polym. Eng. Sci.*, **1978**, 18 (6), 488.
- [4] Peterlin, A., *J. Appl. Phys.*, **1977**, 48 (10), 4099.

- [ 5 ] Yan , R. J. Ph. D. Thesis, Changchun Institute of Applied Chemistry, Academia Sinica, 1989.
- [ 6 ] Prasad, K. and Grubb, D. T., *J. Polym. Sci. Part B: Polym. Phys.* **1989**, 27, 381.
- [ 7 ] Maxfield, J.; Stein, R. S. and Chen, M. C., *J. Polym. Sci. Polym. Phys. Ed.*, **1978**, 16, 37.
- [ 8 ] Derouault; J. L. and Hendra, P. J., *J. C. S. Chem. Comm.*, **1972**, 21, 1187.
- [ 9 ] Snyder, R. G., *Macromolecules*, **1981**, 14, 77.
- [ 10 ] Wool, R. P.; Bretz, R. S.; Li B. Y.; Wang, C. H. and Boyd, R.H., *J. Polym. Sci. Polym. Phys. Ed.*, **1986**, 24, 1039.
- [ 11 ] Strobl, G. R. and Hagedorn, W., *J. Polym. Sci., Polym. Phys. Ed.*, **1978**, 16, 1181.
- [ 12 ] Glotin, M. and Mandelkern, L., *Colloid Polym. Sci.*, **1982**, 260, 182.
- [ 13 ] Glotin, M.; Domszy, R. and Mandelkern, L., *J. Polym. Sci. Polym. Phys. Ed.* **1983**, 21, 285.
- [ 14 ] Hyon, S. H.; Horh, F. and Kitamaru, R., *Bull. Inst. Chem. Res., Kyoto. Univ.*, **1977**, 55(2), 248.
- [ 15 ] Kitamaru, R.; Horii, F. and Nakagawa, M., *Polym. Prepr. ACS*, **1987**, 28, 58.
- [ 16 ] Furuhashi, K.; Yokokawa, T.; Seoul, C. and Miyasaka, K., *J. Polym. Sci. Polym. Phys. Ed.*, **1986**, 24, 59.
- [ 17 ] Peterlin, A. and Corneliussen, R., *J. Polym. Sci.*, **1968**, A-2(6), 1273.
- [ 18 ] Fischer, E. W.; Goddar, H. and Schmidt, G. F., *Makromol. Chem.*, **1968**, 118, 114.
- [ 19 ] Corneliussen, R. and Peterlin, A., *Makromol. Chem.*, **1967**, 105, 193.
- [ 20 ] Meinel, G. and Peterlin, A., *J. Polym. Sci.*, **1967**, B5, 613
- [ 21 ] Peterlin, A. and Meinel, G., *J. Appl. Phys.*, **1965**, 36(10), 3028.
- [ 22 ] Sumita, M.; Miyasaka, K. and Ishikawa, K., *J. Polym. Sci. Polym. Phys. Ed.*, **1977**, 15, 837.
- [ 23 ] Story, E.R. and Hay, J. N., *Polym. Commun.*, **1988**, 29, 9.
- [ 24 ] Onogi, S.; Tanaka, A.; Ishikawa, Y. and Igrashi, T., *Polym. J.*, **1975**, 4, 467.
- [ 25 ] Prevorsek, D. C. and Sharma, R. K., *Polym. Eng. Sci.*, **1974**, 14, 778.