

Diamagnetic Properties of Polyethylene*

2. Analysis of Phase Contributions

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Abstract

A novel approach which accounts for the independent contributions to the specific diamagnetic susceptibility (χ_m) of the amorphous and crystalline phases in, both, the solid and the liquid state of a series of low density polyethylenes (PE) is reported. The dependence of diamagnetism, for each phase contribution, on crystallinity is derived. The much larger rate of increase found for the diamagnetic contribution of the amorphous regions to χ_m is in accordance with the major influence of defects, perturbing the packing of chain segments rejected from the crystals. A parallel discussion for the liquid state favours the occurrence of a local mesomorphic state above the melting point.

Introduction

In the first part of this study (ANIA and BALTA CALLEJA, 1983) the dependence of the diamagnetic susceptibility on temperature and number of chain defects (ϵ) within the lamellar structure of polyethylene (PE) was investigated. The diamagnetism of the solid state of PE with a given number of defects is characterized by a constant value. With increasing temperature, the diamagnetic susceptibility rises gradually, at the beginning of the melting interval, reaching a plateau which defines the diamagnetism of the liquid phase. The percent increase in diamagnetism, $\delta\chi$, of such a change of state was found to be primarily due to an increase of intermolecular disorder within the crystalline segments. It was, further, found that when increasing the proportion of defects within the chain molecules of PE, the molecular packing in the solid state is perturbed, lowering the intermolecular interactions and provoking, as a result, an increase of the diamagnetic susceptibility. Unexpectedly, a similar increase in diamagnetism was also detected in the molten state by the gradual introduction of chain defects, favouring the view of a state of local intermolecular order in molten PE. This local mesomorphic state of order was investigated up to temperatures $\sim 20^\circ\text{C}$ above each melting interval. The occurrence

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of a "local mesomorphic state" above the melting point of n-alkanes and low density PE has, in fact, given rise to certain controversy in recent years (FISCHER et al., 1979; PATTERSON et al., 1983; CLAUDY et al., 1983) Nevertheless Brillouin scattering studies (KRÜGER et al., 1981; KRÜGER et al., 1981), viscosity measurements (PIETRALLA and KRÜGER, 1980) and differential scanning calorimetry data (DENNY and BOYER, 1981) seem to provide a positive evidence for the existence of such a mesomorphic state. A local mesomorphic order is in accordance with theories and results postulating a dense package of chain segments in the liquid polymer state (KARGIN, 1958; YEH, 1972; PECHHOLD and GROSSMANN, 1979).

The object of the present study is to offer a novel approach allowing to distinguish between the separate contributions to the diamagnetic susceptibility of the amorphous and crystalline phases in both, the solid and the liquid state. Since PE crystallizes from the melt as stacks of crystalline lamellae separated by amorphous regions, one may expect a different contribution to the diamagnetic susceptibility from the well ordered crystalline phase and from the disordered amorphous regions.

Results and Discussion

The experimental values, for the specific diamagnetic susceptibility of the investigated samples in part I (ANIA and BALTA CALLEJA, 1983) are shown in Figure 1, as a function of degree of crystallinity (α). The total concentration of defects for these samples ranges from $\epsilon \sim 0.2$ ($\alpha=0.92$) up to ~ 7 defects per 10^2 CH_2 ($\alpha \sim 0.2$). For experimental details see (ANIA and BALTA CALLEJA, 1983). These data can be fitted to a square function of the type:

$$\chi_m = a_0 + a_1\alpha + a_2\alpha^2 \quad |1|$$

with $a_0 = -1.027 \times 10^{-8}$; $a_1 = 3.54 \times 10^{-10}$; $a_2 = -1.58 \times 10^{-10}$.

As the value of α is being controlled by the total number of chain defects (CACKOVIC, et al., 1977) it seems reasonable to choose α as a suitable parameter to express the variations of diamagnetism. We had, in fact, previously shown how the increase in the proportion of chain defects provokes an increase in the diamagnetic susceptibility (ANIA and BALTA CALLEJA, 1983). Thus, high crystallinity corresponds to PE samples having few chain defects. With increasing number of defects (decreasing α) a rising tendency for the diamagnetic susceptibility is detected. Indeed from Figure 1 one obtains a much lower χ_m value for the fully crystalline solid ($\alpha=1$; $\chi_{mC} = -1.007 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$) than for the fully disordered phase ($\alpha=0$; $\chi_{m_a} = -1.027 \times 10^{-8} \text{m}^3 \text{kg}^{-1}$). The

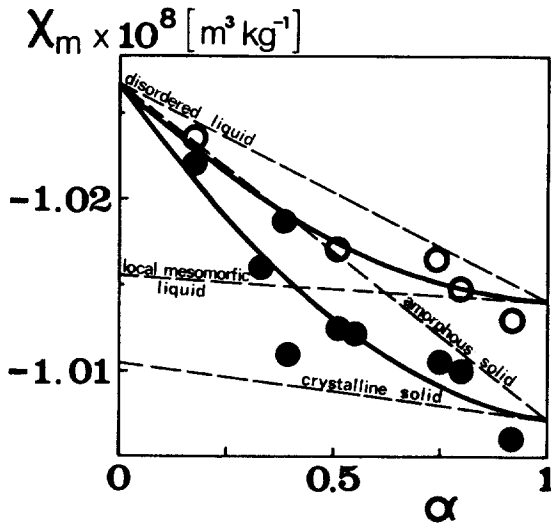


Fig. 1. Plot of diamagnetic specific susceptibility for Polyethylene in the solid (●) and in the liquid (○) state as a function of volume crystallinity. The solid curves are given by equations 2 and 3 assuming a linear dependence of independent microphase contributions (dotted lines)

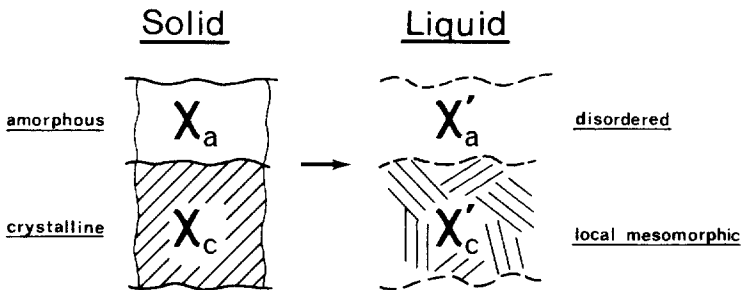


Fig. 2. Schematics of microphase contributions to χ_m . Left: solid lamellar structure having distinct crystalline and amorphous contributions. Right: suggested heterogeneous liquid microphase showing the coexistence of a mesomorphic and a more disordered phase.

increase of χ_m in the solid state (decreasing α) is originated by the thickness decrease of the crystalline lamellae and the concurrent thickness increase of the disordered regions (MARTINEZ SALAZAR and BALTA CALLEJA, 1979). The parallel observed increase of χ_m with decreasing α in the liquid state suggests a persistence of a local mesomorphic microstructure which is still sensitive to the original changes in crystallinity.

Let be, according to the scheme of Figure 2, the contributions to χ_m in the solid state: χ_a and χ_c . In the liquid state two distinct contributions from the local mesomorphic "ordered" and from the "more disordered" regions could also be taking into account (χ'_a and χ'_c).

The additivity of specific susceptibility of the crystalline and amorphous regions in the solid state can be written as:

$$\chi_m = \alpha \chi_c + (1-\alpha) \chi_a \quad |2|$$

In the liquid state the additivity of susceptibilities would be likewise:

$$\chi'_m = \alpha \chi'_c + (1-\alpha) \chi'_a \quad |3|$$

Equations 2 and 3 cannot explain the experimental values given in Figure 1 if χ_c and χ_a (or χ'_c and χ'_a) were assumed to be constant. Hence, we propose a linear dependence of χ_c and χ_a upon α for the solid and the liquid state so that a second degree-equation can be fitted to the experimental data. Thus for the solid state:

$$\chi_c(\alpha) = \chi_c(0) - \alpha(\chi_c(0) - \chi_c(1)) \quad |4|$$

$$\chi_a(\alpha) = \chi_a(0) - \alpha(\chi_a(0) - \chi_a(1)) \quad |5|$$

By substitution of equations 4 and 5 into 2, assuming that for $\alpha=1$, $\chi_m = \chi_c(1)$ and $\chi_a(\alpha) = \chi_c(1)$ we obtain:

$$\chi_m = \chi_a(0) - (2\chi_a(0) - \chi_c(1) - \chi_c(0))\alpha + (\chi_a(0) - \chi_c(0))\alpha^2 \quad |6|$$

By comparing equations 1 and 6 the microstructural coefficients for the solid state, χ_a (amorphous phase) and χ_c (crystalline phase), as a function of crystallinity (dotted lines in Fig. 1) are derived.

For $\alpha=1$, $\chi_c(1) = -1.007 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1}$. This value practically coincides with the previously derived contribution of the

intermolecular interactions to χ_m occurring in chain paraffins (BALTA CALLEJA et al., 1976). Figure 1 indicates that the rate of increase for the diamagnetic contribution of the amorphous regions to χ_m is much larger than that of the crystalline regions. This result is in accordance with the prevailing exclusion of defects from the crystals into the amorphous regions and lateral grain boundaries, contributing to the enhancement of the diamagnetic susceptibility. The small fraction of defects included within the crystals (5-20%) (MARTINEZ SALAZAR and BALTA CALLEJA, 1979) provokes, nevertheless, an expansion of the unit cell which could contribute to the very small increase of $\chi_C(\alpha)$ depicted in figure 2.

A similar treatment to the analysis of data can tentatively be applied (ANIA, 1983) in the liquid state. Accordingly the two dotted lines for the "local mesomorphic liquid" and the "disordered liquid" are shown in figure 2. The diamagnetic contributions in this case show lower slopes than the corresponding ones in the solid state. This result would suggest that the defect inclusion in the polymer chains produces smaller distortions in both liquid microphases.

From the foregoing diamagnetic study of solid and liquid PE we are led to the following CONCLUSIONS:

- 1) In solid laminar PE the diamagnetic contributions to χ_m of crystalline lamellae and disordered regions can be independently evaluated.
- 2) A quadratic dependence of diamagnetism on crystallinity for each physical state is derived. It entails a diamagnetic additivity of microphases.
- 3) The analysis of the diamagnetic susceptibility of the molten state points to the existence of a local mesomorphic state as a constituent of a heterogeneous liquid phase, in accordance with other above mentioned models (KARGIN, 1958; YEH, 1972); PECHHOLD and GROSSMANN, 1979). This mesomorphic microphase occurring in the vicinity of the melting point, tends to be destroyed with the gradual incorporation of chain defects.

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