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E.p.r. study of the orientation of polymer segments induced by cold drawing of a low density polyethylene

V. Strauch* and M. Schara
J. Stefan Institute, University of Ljubljana, Ljubljana, Slovenia
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The orientation of low density polyethylene (LDPE) chain segments induced by cold drawing was determined by electron paramagnetic resonance spectra measured for samples probed by tempyl stearate or alkyl radicals formed by γ-irradiation. We characterized the induced orientation in the amorphous phase using a two-dimensional Gaussian distribution function ($\sigma = 12°$), axially symmetrical about the draw direction. A simultaneously induced alignment of the crystallite c-axes with the draw direction, accompanied by a random orientation of the crystallite a-axes and b-axes, was also observed. We propose that the molecular morphology of cold-drawn LDPE can be described in terms of specifically oriented crystallites emanating chain segments packed in the condis state.

(Keywords: cold drawing; condis state; draw direction)

INTRODUCTION

An applied mechanical stress affects the molecular conformation of the macromolecules in polymers by different mechanisms. Thus the cold drawing of polymers consists of a complex combination of chain fracture, void formation and crazing along with molecular orientation and oriented fibril effects[1]. Which mechanism will prevail is closely connected to the molecular morphology[2] of the studied polymer. The morphology of polyethylene concerning the organization of macromolecules in the lamellae and the amorphous part through chain folding has been a matter of debate for several decades, culminating in 1979[3]. It seems now to be satisfactorily explained by the gambler's ruin model, based on the statistics of random walks[4,5], but this model still needs to be experimentally proven.

The drawing of semicrystalline polymers has been studied intensively. Peterlin's molecular model of drawing for polyethylene and polypropylene[6,7] is accepted as generally true[8,9], despite the old controversies related to the molecular morphology of semicrystalline polymers. Common to all findings of polyethylene structure–property relationships studies is the ambiguity concerning the amorphous–crystalline phase relationship of the polymer when exposed to various mechanical deformations.

It is well known that nitroxide spin probes introduced into polyethylene reside in the amorphous phase[10–12]. The proper selection of a nitroxide spin probe which can align with its long molecular axis together with the polymer chain segments allows us to determine the chain segment orientation via the anisotropy of g and the hyperfine tensors of the unpaired electron. On the other hand, the electron paramagnetic resonance (e.p.r.) spectra of relatively stable, γ-irradiation-induced alkyl radicals in low density polyethylene (LDPE) can only be measured for the crystalline phase[13]. The anisotropy of the hyperfine splitting for α-protons and β-protons reveals the orientation of the crystallographic axes[14] c, a and b.

By analysing the angle dependent e.p.r. lineshapes of the introduced nitroxide spin probe molecules and trapped alkyl radicals in cold-drawn LDPE, the induced orientation of the chain segments in the amorphous and crystalline phases as well as the amorphous–crystalline morphological relationship can be determined.

EXPERIMENTAL

Low density polyethylene (LDPE) type Okiten F21 (obtained from Dr Veksli at the Ruđer Bošković Institute, Zagreb, Croatia) was used. The crystalline content was 60% as determined by X-ray diffraction following the method described elsewhere[15,16]. The LDPE samples were probed with less than 0.02% tempyl stearate (1-oxyl-2,2,6,6-tetramethyl-4-stearyloxycarbonylpiperidine, obtained from Professor Pečar, University of Ljubljana, Slovenia) by immersion for 12 h in a 10^{-3} M solution of the probe in benzene at 60°C. The solvent was distilled away at 40°C. The doped samples were then dried for 24 h at 70°C and 2 kPa vacuum. Afterwards, they were transferred to the DIN melting index determining apparatus, heated at 180°C for 3 min and hydrostatically injected into 4 mm wide rod-shaped moulds using a 21.6 kg weight.

The injected rods, cooled to room temperature, were

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* To whom correspondence should be addressed

slowly stretched under 150–220 N load to a 500% elongation in an Instron tensile testing machine. The stretched items remained further clamped within the machine grips until the load decreased to below 10 N, and were then unclamped and left at room temperature for a week.

A 4 mm long cylindrical sample cut from the stretched item was fastened with a Teflon band onto the flat end of the e.p.r. glass tube and mounted in the goniometer opening. This goniometer assembly was then put in the microwave TE_{102} resonant cavity so that the sample could be positioned with its draw direction axis parallel or perpendicular to the external magnetic field.

The chemical stability of tempyl stearate was checked by comparing its e.p.r. intensities after drying, hydrostatic injection and cold drawing of the probed samples. No significant degradation of the probe was found.

We formed the alkyl radicals in the stretched LDPE samples using γ-irradiation at liquid nitrogen temperature. The total absorbed dose was 10^4 Gy (1 Gy = 100 rad). The irradiated samples were exposed to higher temperatures for the 15–20 s needed to position them in the 173 K precooled resonator. The e.p.r. spectra were measured with the same sample axis position as for the tempyl stearate experiments.

All spectra were measured on a Bruker ESP 300 e.p.r. spectrometer equipped with a variable temperature controlling unit and a goniometer. For the e.p.r. measurements of the samples doped with tempyl stearate we used an external magnetic field range of 343.22–353.22 mT, a microwave frequency (at 20 mW power) of 9.78 GHz, a receiver gain of 2×10^5 and a modulation amplitude (at 100 kHz) of 0.2 mT. The spectra, each of 2048 digital points, were averaged over 10 accumulations. For the samples doped with alkyl radicals we used an external magnetic field range of 331.5–351.5 mT, a microwave frequency (at 20 mW power) of 9.60 GHz, a receiver gain of 6.3×10^4 and a modulation amplitude (at 100 kHz) of 0.2 mT. The spectra, each of 4096 digital points, were averaged over 200 accumulations.

The e.p.r. intensity of tempyl stearate in injected and cold-drawn samples varied within ± 5%. This variation is within the reproducibility range of e.p.r. measurements and proves that no significant amount of the probe degraded during our experiments. We also found good reproducibility of the e.p.r. lineshape and intensity in the cold-drawn samples after several cooling and heating cycles between 273 and 173 K. Irreproducibility of the e.p.r. lineshape was found only for the sample heated to 373 K[17].

The e.p.r. lineshapes for tempyl stearate were calculated using a program written in Microsoft FORTRAN 5.0 running on a PC. The program was tested for calculation precision on a VAX computer. Its ability to reproduce the real e.p.r. lineshape was proven for a tempyl stearate powder sample. The basic program algorithm involves a joint probability formula, where a two-dimensional, axially symmetrical Gaussian function was used for the statistical weight of the sine law.

The components of the tensor g, in principal axes notation, used in our spectral calculations were taken for tempone (1-oxyl-2,2,6,6-tetramethyl-4-oxopiperidine) from Gaffney[18]. These components, together with those used for the hyperfine splitting A (in millitesla), are

$$\begin{gathered} g = \begin{vmatrix} 2.0104 & 0 & 0 \\ 0 & 2.0074 & 0 \\ 0 & 0 & 2.0026 \end{vmatrix} \\ A = \begin{vmatrix} 0.56 & 0 & 0 \\ 0 & 0.56 & 0 \\ 0 & 0 & 3.3 \end{vmatrix} \end{gathered} \tag{1}$$

A Lorentzian lineshape 0.6 mT wide was chosen.

The thermal properties of the samples were studied using a Perkin–Elmer DSC-4 differential scanning calorimeter. The scan rate was 10°C min^{-1}. The injected and stretched samples were cycled once between −40 and 140°C.

RESULTS AND DISCUSSION

The amounts of the crystalline phase in the injected and cold-drawn polymer were determined from the heats estimated from the differential scanning calorimetry (d.s.c.) curves (*Figure 1*) using the melting heat data for crystalline polyethylene[19]. The d.s.c. results reveal that the injected sample contained 5% less crystalline phase than the cold-drawn one. Both samples showed no difference in the crystallization enthalpy after going through the cooling cycle.

The e.p.r. spectra were measured at 173 K to avoid α-, β- and γ-transition interference as observed for linear and branched polyethylenes[20]. At this temperature, e.p.r. lineshape modulation by motional averaging of g and hyperfine tensor components was avoided. Both the

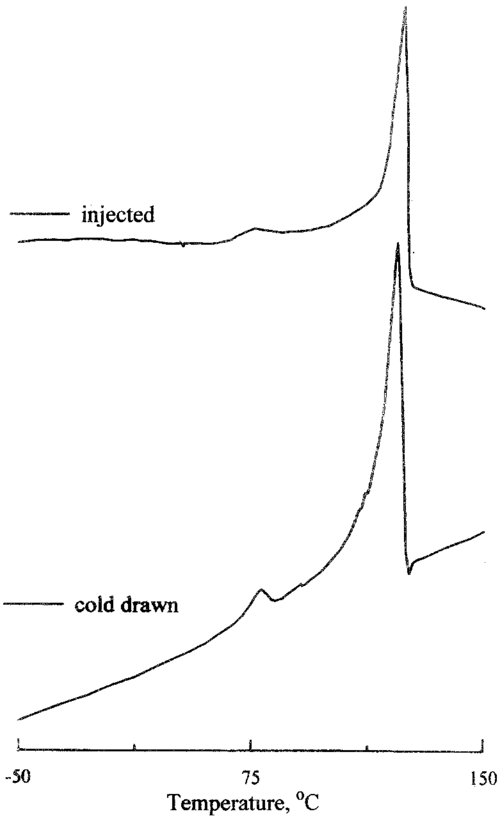

Figure 1 D.s.c. curves measured for the injected and cold-drawn polyethylene samples at a heating rate of 10°C min^{-1}

Figure 2 Experimental and calculated e.p.r. spectra of tempyl stearate for the polyethylene sample with the draw direction axis parallel to the external magnetic field

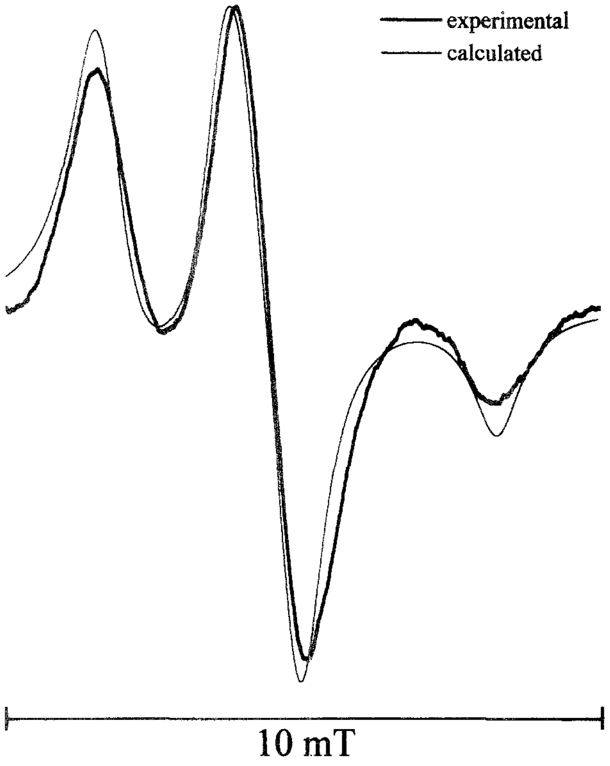

Figure 3 Experimental and calculated e.p.r. spectra of tempyl stearate for the polyethylene sample with the draw direction axis perpendicular to the external magnetic field

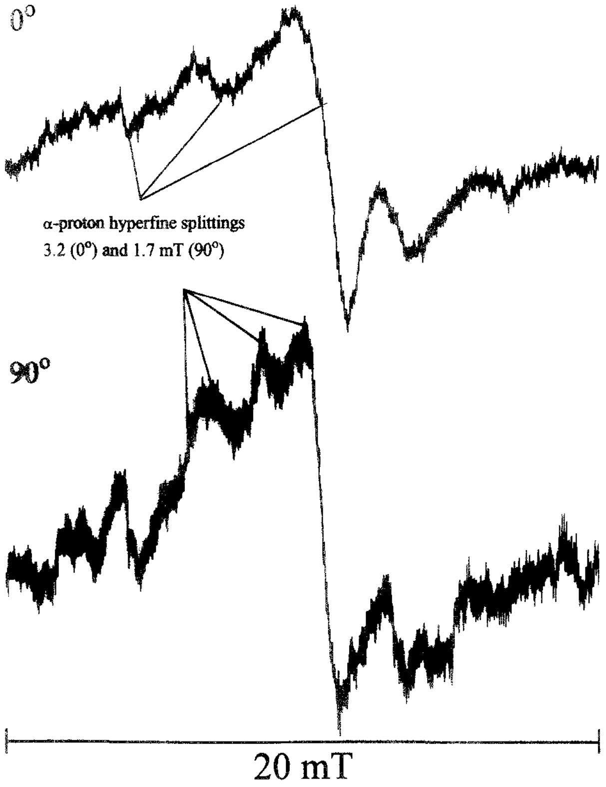

Figure 4 E.p.r. spectra of the alkyl radicals measured for the γ-irradiated polyethylene samples positioned parallel (0°) and perpendicular (90°) to the external magnetic field

transitions and motional averaging could shadow the orientational effects induced by cold drawing.

Our previous study using different nitroxides showed that fatty acid derivatives are the most suitable nitroxide spin probes to characterize the orientation of polyethylene chain segments induced in the cold-drawn polymer[17,21]. Among them, tempyl stearate was found to align its long molecular axis with the direction of the extended polyethylene segments. The magnetic symmetry axis of its nitroxide unpaired electron is perpendicular to its long molecular axis and the piperidine ring plane. Such anisotropic spin probe structure enables measurement of different molecular orientations.

In analysing the experimental e.p.r. lineshape for the cold-drawn sample positioned with its draw direction axis parallel to the external magnetic field, we found, besides the lineshapes related to the oriented tempyl stearate molecules, some 10% of the powder pattern. This pattern originated from the disordered polymer sites, most probably located in the crystalline–amorphous phase interfacial regions.

A two-dimensional, axially symmetrical Gaussian distribution function with $\sigma = 12°$ was chosen to describe the induced orientation of the chain segments in the amorphous part. The value of σ was determined from the best fit of the experimental and calculated normalized spectra shown in *Figure 2*. The best fit was quantified by the least square of the difference between both spectral amplitudes.

Wilke and Bratrich[22] determined a value of 10° for σ using synchrotron radiation for LDPE stretched uniaxially at a drawing temperature of 353 K. Despite the different methods used, both values of σ are in remarkable accordance. This shows that the structural element, the long molecular axis of tempyl stearate, used in our study to define the orientation distribution function of the chain segments is well justified.

There was additional information about the chain orientation obtained when the spectra were measured with the sample draw direction axis perpendicular to the external magnetic field (*Figure 3*). The best fit was only achieved if we considered the probe molecules to be additionally oriented by having their piperidine rings axially symmetrical about the draw direction. This confines the unpaired electron magnetic symmetry z-axis of the probe molecules to an angle $\pi/(2-\theta)$ with the draw direction, where θ is the polar angle between this direction and the long molecular axis. Such an additional molecular arrangement relates to a specific LDPE molecular morphology, where the insertion of the probe conforms with the hexagonal packing of the polymer chain segments. This orientational state is known as the conformationally disordered (condis) state[23].

The orientation of the crystallites in the draw direction was assessed from the angle dependent e.p.r. spectra of the alkyl radicals, shown in *Figure 4* for the γ-irradiated samples positioned parallel (0°) and perpendicular (90°) to the external magnetic field. The measured spectra could be assigned only to those alkyl radicals trapped in the polyethylene crystalline phase, which is in agreement with the findings of other authors[24,25].

The hyperfine splitting of the α-proton determined from the 0° spectrum in *Figure 4* and measured in the irradiated sample positioned parallel to the magnetic field was found to be 3.2 mT. This value is close to the splitting of 3.4 mT observed by Shimada *et al.*[14] for alkyl radicals in polyethylene crystallites with ideally oriented c-axes, which indicates that in our sample a partial orientation of the crystallite c-axes in the draw direction was achieved. However, the hyperfine splitting of the α-proton determined from the 90° spectrum in *Figure 4* for the perpendicular sample position was 1.7 mT. The observed splitting shows, compared to the value reported elsewhere[14], that the crystallites in our samples are randomly oriented with regard to their a-axes and b-axes.

We propose that the molecular morphology of cold-drawn LDPE can be described as consisting of specifically oriented crystallites emanating chain segments packed in the condis state.

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