Diamagnetism and Structure of Nitric Acid-Treated Bulk Polyethylene

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Summary

An alternative procedure to examine the nature of the end product of nitric-acid-treated bulk polyethylene involving the measurement of the diamagnetic suscepti- bility is reported. This simple non-destructive method complements previous results obtained by means of IR spectroscopy. Thus after selectively removing the sur- face layer of the polyethylene lamellae with nitric acid (t > 50h) the diamagnetic susceptibility substan - tially decreases to values which are consistent with tilted paraffinic chains terminated by carboxyl groups including $-NO_2$ groups in a 4:1 ratio.

Introduction

In previous studies (PHAOVIBUL et al., 1973) the value of diamagnetic susceptibility, χ_m, as a tool for the structure analysis of polymers was emphasized. The use of semiempirical diamagnetic increment systems (MULAY and BOUDREAUX, 1976) permits, in addition, a number of structural chemical examinations and a separation of intra from intermolecular contributions to χ_m (BALTA CALLEJA et al., 1965). In particular the susceptibili- ty study of paraffinic monodisperse homologous series furnishes valuable data on the independent contribu - tions from the backbone and from the chain ends to the susceptibility (BALTA-CALLEJA et al., 1976). The purpo se of this work is to report the measurement of the diamagnetic specific susceptibility of the end products which result after selective oxidation of melt crysta- llized polyethylene treated with nitric acid. These values have been compared with experimental data on di carboxylic acids and paraffins and those derived from increment systems to analyse the nature of the degraded molecular chains and the amount of oxidized groups in- troduced by the etching treatment.

Experimental

The total defect content (branches plus unsaturations) and the defect content within crystals (CAGIAO et al., 1980) for the polyethylene samples investigated are collected in Table I. The nitric-acid degradation was performed at 60°C in open tubes during reaction times

t > 50h. Further details concerning the preparation and characterization of the samples are described elsewhere (RUEDA et al., 1981). For the magnetic study the Faraday method was employed. The samples, in powder form, were tightly packed in quartz tubes (inner diame - ter 4 mm; height 8 mm). The tubes were placed in a double cylinder of glass in which a thermostated liquid is circulated between the constant B $\partial B/\partial x$ pole caps of a B-M 6 Bruker electromagnet. The force acting on each sample, typically weighing 10^{-4}kg, is of the order of 10^{-5}N for the maximum applied magnetic field (~ 1.5T). For the elimination of any effects due to ferromagnetic impurities, χ_m values were obtained from a (χ_m, $1/B$) plot by extrapolation of $B \to \infty$. Each sample was measured ten times at two different field strenghts in a vacuum of 1.5 Pa. At a 0.03 m gap between pole caps the B $\partial B/\partial x$ values for 20A are respectively: 12.32 and 21.69 $T^2 m^{-1}$. In order to compare the treated polymer samples with solid dicarboxylic acids, a series of commercial (Merck) diacids were also investigated. They follow the general expression: $(COOH-(CH_2)_n-COOH)$; n = 2,4,5,6,8,10 and their χ_m values (Fig. 1, full circles) have not yet been reported before. Melting points were determined with a Perkin-Elmer DSC-1B differential scanning calo- rimeter at a heating rate of 8°C/min.

Results and Discussion

The basis of the discussion lies on the selectivity of the nitric acid reaction. It has been previously proved that with the selected degradation times the disordered material was fully digested (CAGIAO et al., 1980). Since the majority (> 80%) of chain defects (butyl or larger) lie admittedly on the non crystallized regions, the end product after degradation consists mainly of paraffinic chains, terminated by heavy groups with a small defect content $\varepsilon_c < 0.01$ within the crystal. The average crys- tal thickness of the end product was calculated by ta- king into consideration the existence of two predomi - nant lamellar thicknesses which are evidenced from the double melting temperature DSC peak in samples 1 and 2. Sample 3 shows only one single peak suggesting that only crystals with the larger thicknesses persist after the attack. The crystal thickness, ℓ_t, was deduced from: $\ell_t = 2\sigma_e T_m^o/(\Delta T \Delta h_c^\infty)$ where $\sigma_e = 7.9 \times 10^{-2}$ J m^{-2}; $T_m^o = 418.5$ K; $\Delta h_c^\infty = 2.8 \times 10^8$ J kg^{-1}. This expression has been previous- ly shown to hold in case of nitric acid treated polye - thylene (ILLERS, 1968 ; MEINEL et al., 1970). The ave - rage crystal thickness ℓ_t was finally derived from the ratio between the areas of both DSC peaks. The molecu- lar length L has been further calculated from L=$\bar{\ell}_t$/sinϕ assuming a chain tilt of $\phi \cong 34$? Electron diffraction results (KELLER and UDAGAWA, 1971) from nitric acid isolated lamellae and electron microscopical observa - tions on chlorosulfonated polyethylene (KANIG, 1981)

TABLE I

Defect content ε, defect content within crystals ε_c, crystal thicknesses ℓ_t, molecular length L, average number $\bar{n}$ of repeating $-CH_2-$ units and specific susceptibility (before, χ_m^b and after treatment, χ_m^a) of the samples of polyethylene.

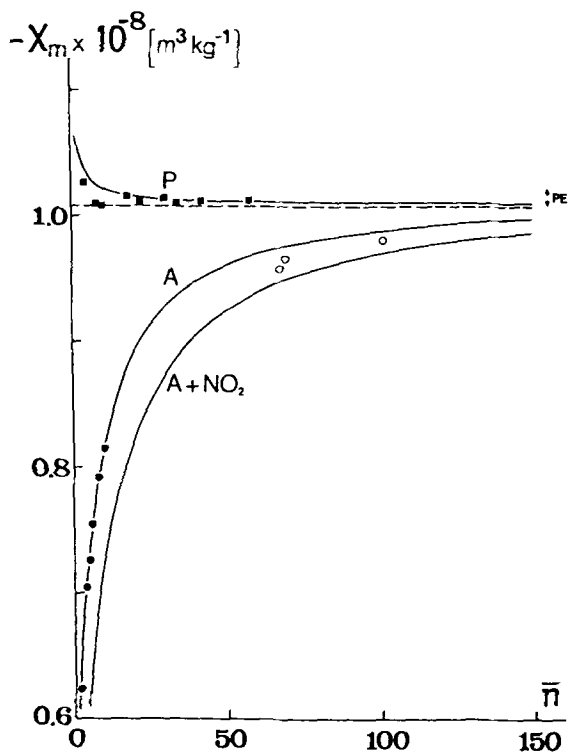| Sample	ε (%)	ε_c (%)	ℓ_t (nm)	ℓ_t (nm)	L (nm)	$\bar{n}$	$-\chi_m^b \times 10^{-8}$ ($m^3 kg^{-1}$)	$-\chi_m^a \times 10^{-8}$ ($m^3 kg^{-1}$)
1	1.81	0.79	12.8 9.1	10.6	12.8	101	1.010±0.001	0.981±0.003
2	3.49	0.83	8.5 6.0	7.3	8.8	69	1.012±0.001	0.966±0.003
3	6.90	0.96	7.2 —	7.2	8.7	68	1.022±0.001	0.956±0.003

Fig. 1. Diamagnetic specific susceptibility as a func - tion of the number $\bar{n}$ of repeating $-CH_2-$ units. The hyperbolic curves correspond respectively to paraffins (P), dicarboxylic acids (A) and dicarboxylic acids including a $-NO_2$ groups per molecule ($A + NO_2$). All sym - bols correspond to experimental values: (■) solid paraffins; (●) solid dicarboxylic acids; (O) treated PE.

confirm this tilt. Hence, the number $\bar{n}$ of repeating
$-CH_2-$ units within the crystalline stems is $\bar{n}=L/0.127$,
where 0.127 nm is the $-CH_2-$ projected length. Table I
gives the ℓ_t, ℓ_t, L and $\bar{n}$ values and the values of the
specific susceptibility χ_m of the polyethylene samples
investigated before and after nitric acid treatment.
The χ_m substantial decrease after treatment is evident.
The χ_m values for the treated samples are represented
by open circles in Fig. 1. The hyperbolic curves corres
pond respectively to the specific diamagnetic suscepti-
bility values of a series of paraffins (P) in the solid
state (BALTA-CALLEJA et al., 1976), dicarboxylic acids
(A) and dicarboxylic acids including a $-NO_2$ group per
molecule $(A + NO_2)$. These curves follow the general
expression:

$$\chi_m = \frac{n\,\chi_p + b_p}{nM_1 + M_2} \quad \text{where} \quad \chi_p \simeq 1.42 \times 10^{-10}\,m^3\,mol,$$

represents the contribution to the molecular diamagne -
tism of the $-CH_2-$ group and b_p is the contribution
associated to the end groups ($b_p = -3.27 \times 10^{-10}$, $-4.54 \times$
10^{-10} and $-5.54 \times 10^{-10}\,m^3\,mol^{-1}$ for P, A and $A+NO_2$ respec
tively). M_1 and M_2 are the molecular masses for a $-CH_2-$
group and the corresponding end groups respectively.
The P and A curves were calculated from the experimental
values of solid paraffins (full squares) and solid di -
carboxylic acids (full circles). The curve $A+NO_2$ has
been calculated from the susceptibility increments
assuming that each molecule is a dicarboxylic acid inclu
ding one NO_2 group. It is noteworthy that the suscepti-
bility values obtained from any increment system are
frequently higher than the experimental values in the
solid state. This is because such increment systems do
not include intermolecular interactions. However, in
the case of dicarboxylic acids, curve A practically
coincides with the one calculated from the increments'
method. As $n \to \infty$, $\chi_m \simeq \chi_p/M_1$, i.e. the hyperbolae assimp-
totically approach the χ_m value of an infinite paraffi-
nic chain (straight dotted line in Fig. 1). It is seen
that the experimental values of treated polyethylene
(open circles) are lying below curve A and well below
curve P. This result confirms, that for long treatment
times (> 50h) the paraffinic character of the molecular
chains is lost and the crystals consist mainly of chains
terminated by COOH groups. The presence of ~1% chain
defects per 10^2 CH_2 within the crystals does not seem
to affect the χ_m value. This value is, however, some -
what elevated in case of chain systems containing back-
bone defects (ANIA et al., 1979). In our case the con-
centration of defects is probably too low to be detec-
ted by magnetic susceptibility. Otherwise this χ_m value
would fit with the view of stems containing branches
within the crystals as almost perfect space filling

point defects. The observed depression of magnetic sus
ceptibility from curve A (dicarboxylic acids) could be
explained by the introduction of additional groups
which contribute to a lowering of the susceptibility
value. IR data (RUEDA et al., 1981) suggest the nitro
group as the most probable candidate. The experimental
susceptibility data lie between curves A and $A + NO_2$.
Hence, it can be concluded that one nitro group every
two molecules i.e. a ratio of nitro to carboxyl groups
of 1:4, occurs. In summary, the present study offers
new aspects of the degradation mechanism of PE with
FNA highlighting the diamagnetic susceptibility method
as capable to detect with certain detail the drastic
change from the initial two-phase PE structure into
the final paraffinic system and to furnish a separate
confirmation on the nature of oxidized groups.

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