Thermo-Oxidative Degradation of Polyolefines
11. Comparison of Polyethylene Oxidation in Solution and in Melt

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SUMMARY
        Autooxidation of low density polyethylene has been studied
in melt and in 1,2,4-trichlorobenzene solution. The kinetics of
oxygen-absorption, concentrations of hydroperoxides, carboxyl,
and other oxo groups and average number of scissions have been
investigated. It has been found that the main features of the
oxidative processes in solution and in melt do not differ signifi-
cantly. However, the concentration of hydroperoxides as a func-
tion of conversion and the dependence of the maximum concentra-
tion of hydroperoxides on temperature make exception. There is a
very good agreement between average number of chain scissions
and carboxyl groups and this is independent of phase, concent-
ration, temperature, and conversion. From one mole consumed
oxygen approximately $0.6 \div 0.7$ mole remains in the polymer back-
bone in the form of oxygen-containing functional groups. The
ratio of average chain scissions to the formed carbonyl groups
is 1:5, i.e., functional groups form both at the chain ends, in
consecutive reactions after the scission, and along the polymer
chain.

INTRODUCTION
        The oxidation of polyolefins has been investigated mainly
in solid state or in melt, in the expectation to find relation-
ships effectively applicable for manufacturing and application
circumstances. However, the authenticity of results is question-
able because of the poor reproducibility of initial conditions,
e.g., the chemical and physical structure, the thickness of the
polymer. These difficulties may be avoided if the oxidation is
carried out in a suitable solvent; it is, however, questionable
how well the results obtained in solution characterize solid
state or melt oxidation.
        Earlier the oxidation of solid or molten polyolefines was
discussed exclusively on the base of the mechanism which has
been developed to describe the oxidation of low molecular weight
hydrocarbons. This mechanism has also been applied, e.g. by BAWN
and CHAUDRI (1968), to describe oxidation of polypropylene solu-
tions. Decomposition of the polymer-hydroperoxide transition
product is one of the most important steps of oxidation. For
polyethylene, the rate constants of this step were found not to
differ significantly in solution and film samples (ZOLOTOVA,
DENISOV 1970). However, several features of polyolefin oxidation

have also been noted which were dissimilar in solution and in solid state or melt. Some bimolecular elementary processes are favoured in solution, for higher mobility in the less viscous medium (DENISOV 1978, DENISOV and GRIVA 1979). During polyolefin oxidation, both in solution and in condensed phase, oxygen containing functional groups form and the macromolecule undergoes scission. Several authors (OSWALD and TURI 1965, HOLMSTRÖM and SÖRVIK 1974, CHIEN and KIANG 1980, ADAMS 1970) have postulated that the chain scission process of the polymer occurs via β-scission of alkoxy radicals formed during homolysis of polymer-hydroperoxide and polymer-alkylperoxide intermediates. Others (IRING et al. 1980, TROFIMOVA et al. 1981) believe that also the chain scission occuring during transformation of polymer-peroxy radicals is to be significant.

It seems that the literature is not uniform in respect to the connection between processes of functional group formation and scission. Thus, e.g., ADAMS (1970) has claimed that in isotactic polypropylene both formed chain ends contain oxo group while according to OSWALD and TURI (1965) only one of the chain end does. Chain scission of polyethylene and polypropylene followed by formation of double bond at the chain end has recently been pointed out (TROFIMOVA et al. 1980) in contrast to earlier observations (CHENG et al. 1976).

This paper concerns kinetics of formation of certain oxygen containing groups and changes of molecular mass during polyethylene (PE) oxidation in solution and in melt. 1,2,4-trichlorobenzene (TCB) was used as solvent which may be considered to be inert under the used experimental conditions.

EXPERIMENTAL

Low density PE: Preparation of powder or film samples, free from additives, has been described earlier (IRING et al. 1974);
TCB: Extracted by sulfuric acid, then distilled.
Oxidation conditions: Temperature: 160 and 170°C. Film samples: 25 ± 5 μm film thickness, 100 kPa oxygen pressure. Solution: 0.7-2.8 mole/dm^3 PE concentration, 75 or 67 kPa oxygen partial pressure. (Oxygen pressure is not rate determining under these conditions, see IVANCHENKO et al. (1969), KELEN et al. (1976)). For subsequent analysis the solution was cooled and the resulting suspension applied.
Experimental techniques have been described earlier (IRING et al. 1974, 1979). Overall oxygen uptake (Z), overall IR-absorption of carboxyl and other carbonyl groups (T_{CO}) (measured on KBr pellets made after removal of the solvent), concentrations of carboxyl- (A) and hydroperoxede (Y) groups, and molecular mass distribution were measured. Knowing T_{CO} and A, the integral absorption (T_K) and concentration of carbonyl groups (calculated as ketones, K) were evaluated. For these calculations, extinction coefficients $E_K = 6\ 880 \pm 770$ cm mmole^{-1} and $E_A = 16\ 800 \pm 2\ 400$ cm mmole^{-1} were used, values determined using PE stearone and PE stearic acid mixtures.

RESULTS

Rate of overall oxygen uptake is significantly lower in solution than in melt (see Fig.1.), mainly due to the appr. 60 fold difference in polymer concentration. The character of the kinetic curves is, however, the same. The maximal rate of
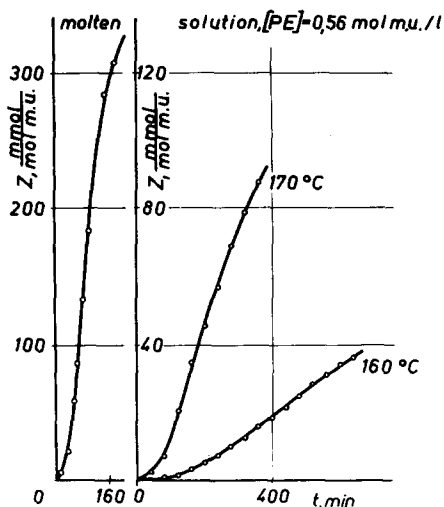
Fig.1. Kinetic curves of oxygen
uptake

oxygen uptake ($W_{Z,max}$) as a
function of polymer concen-
tration (using a logarithmic
scale) gives a straight line
which fits also the data ob-
tained for the melt. This
means that the concentration
dependence of $W_{Z,max}$ is not
affected by viscosity; the
virtual "order" is near to 2.

The change of hydroperoxide
content as a function of ab-
sorbed oxygen (conversion)
can be seen in Fig.3. In bulk
oxidation the hydroperoxide
concentration curve exhibits
a maximum at low conversions
and then falls rapidly. In
solution oxidation it reaches
a long plateau, with much
lower Y values in the whole
conversion range studied. The
decline of the Y curve, i.e.,
the enhanced decomposition of the hydroperoxides may be caused
by the neighbouring functional groups. In solution experiments
the final conversion was not so high, thus the concentration of
hydroperoxides with such neighbours is negligible.

A further difference
is, that while $W_{Z,max}$ inc-
reases monotonously with
temperature, Y_{max} increases
with temperature only in
solution but not in melt
(see data of Table 1).

The concentration de-
pendence of Y_{max} is the
same for both cases (IRING
et al. 1974, 1979)

$$Y_{max} = \frac{2fk_{21}^2}{k_3k_4}[PE]^2 \qquad (1)$$
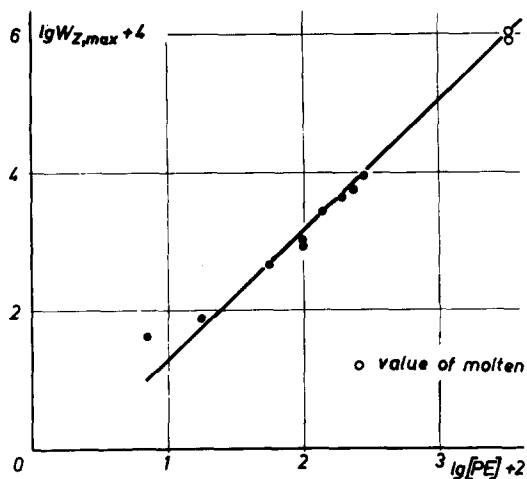
Fig.2. Dependence of maximal rate of
oxygen uptake on PE concentration

where k_{21}, k_3 and k_4 are
the rate constants of pro-
pagation, branching and
termination, respectively
and f is the cage factor
($0 < f < 1$) of hydroperoxide
decomposition. In the melt,
the activation energies for
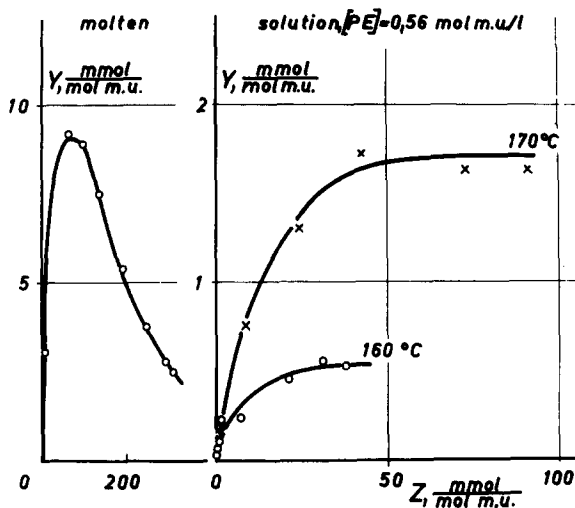k_{21}^2 and k_3k_4, resp., are
nearly equal and this re-
sults in temperature independence of Y_{max}. This similarity seems
not to hold for solution.

The formation kinetics of acidic (A) and carbonyl groups
(K) have been studied (the concentrations given in Figs. 4 and
5 are related to the number average molecular mass of the

Fig.3. Concentration of hydroperoxides (Y) as a function of oxygen uptake (Z)

unoxidized macromolecule $\overline{M}_{n(o)}$). As illustrated in these figures, conversion dependence of both quantities is linear with good approximation, independently of reaction conditions - phase, polymer concentration, temperature.

Although the IR absorption method is widely used for determination of overall concentration of carbonyl groups of polyolefins, results obtained by this method may be only semiquantitatively treated, because of technical and calibration difficulties. Titrimetric analysis of carboxyl groups produces well reproducible data. Joint application of the two methods approximates the overall quantity of oxygen built into polymer (O_p) more exactly.

Table 1.
The maximum rate of oxygen uptake and the maximum hydroperoxide concentration in solution and melt oxidation of PE

	Melt				Solution	
	130°C	140°C	150°C	160°C	160°C	170°C
$[PE], \frac{mmol}{l}$		32.9			0.56	
$W_{Z,max}, \frac{mmol}{mol\ min}$	0.22	0.55	1.34	3.36	0.074	0.30
$Y_{max}, \frac{mmol}{mol}$	7.60	6.72	9.40	9.40	0.56	1.66

O_p was approximated by the relationship:

$$O_p \sim Y + A + \frac{1}{2}K, \text{ mmol } O_2/\text{mol m.u.} \qquad (2)$$

As shown in Fig.6, O_p depends only on conversion, and shows no significant differences in solution and in melt. It seems that in contrary to our earlier assumptions (IRING et al. 1974) and other data (KUZ'MINSKII 1966), more than a half of absorbed oxygen remains in the polymer (mainly in the form of carbonyl compounds) and, in accordance with the data of CHENG et al. (1976), a lesser part leaves the system as water and other volatile materials. It is probable that the formed peroxy radicals, the primer products of the oxidative chain reaction, participate in several competitive chain propagation steps beside the
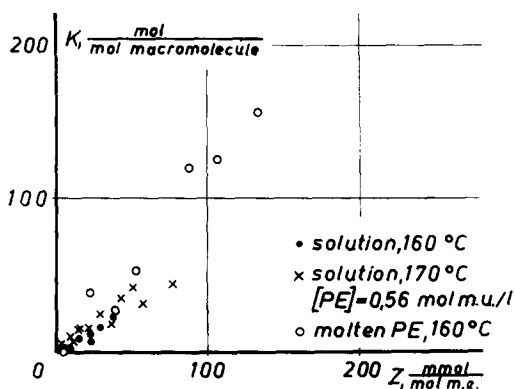
Fig.4. Average number of noncarboxylic
       carbonyl groups (K) as a function
       of oxygen uptake

hydrogen abstraction re-
sulting in formation of
hydroperoxides.

We have previously
assumed that during poly-
ethylene oxidation the
peroxy radicals transform
and yield a carboxyl
group and a hydrocarbon
radical. In this process
both oxygen atoms of the
peroxy radical remain in
the polymer chain; this
is in good agreement with
the result presented in
Fig.6.

We have examined the
change of molecular mass
distribution and calcu-
lated the average number
of scissions for one
macromolecule (s). Like

the conversion dependence of K and A also the s vs. Z function
can be approximated by a straight line, both in melt and in
solution, as illustrated in Fig.7.
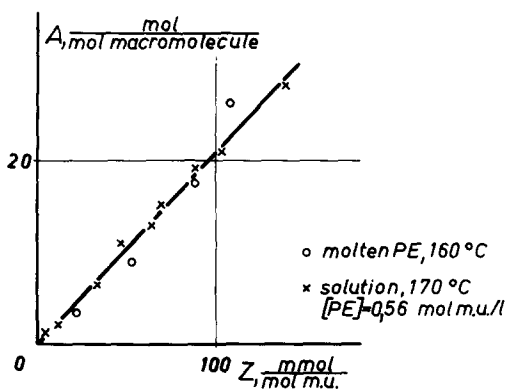
Fig.5. Amount of carboxylic groups (A)
       plotted against oxygen uptake (Z)

If we compare Fig.5 and 7,
the similarity of A vs. Z and
s vs. Z functions is conspicu-
ous. As Fig.8 shows, the
number of carboxyl groups and
that of the chain scissions
are almost the same at the
same conversion.

Temperature independence
of the A/s ≈1 relationship
for PE oxidation in melt has
been previously pointed out
(IRING et al. 1980); the data
presented here prove the con-
centration independence as well.
Thus the formation of acids
and the chain scission are
closely connected.

If we consider the slopes
of the K, A and s vs. Z
straight lines, we obtain that

the ratio (K+A)/s is about 5, in contrast to polyporpylene where,
e.g., ADAMS (1970) has found two oxo groups per chain scission.
According to our finding the polymer chains contain carbonyl
groups also along the chain. Comparing CHENG's data (CHENG et
al., 1976) on functional groups to our scission data at the same
conversion, we obtain the same ratio, oxygen containing groups/
scission ≈ 5. Although the agreement is excellent, we
have to emphasize that, in general, mechanism and functional
group formation rate depend on reaction conditions and conver-
sion.

On the other hand, based on the presented experimental
data, it may be stated that the main features of PE solution
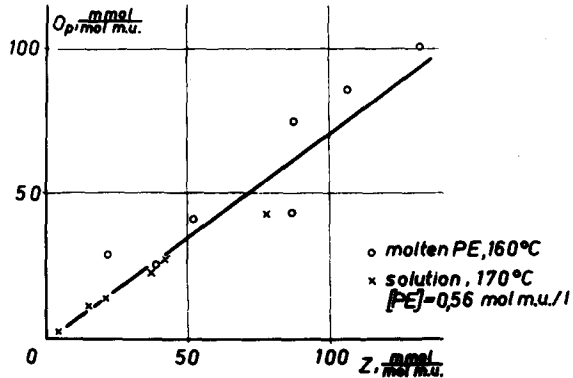and melt oxidation do not whow significant differences.

Fig.6. Amount of oxygen built into the polymer
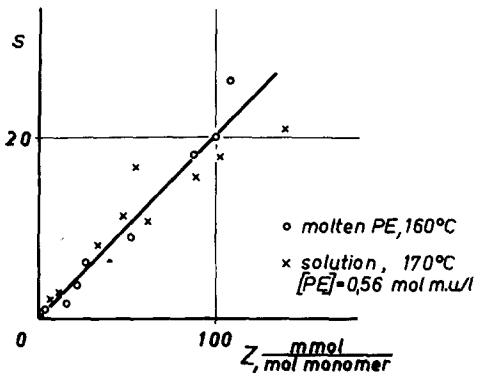(O_p) as a function of the overall
oxygen uptake (Z)

Fig.7. Average number of chain
scissions (s) vs. oxygen
uptake (Z)
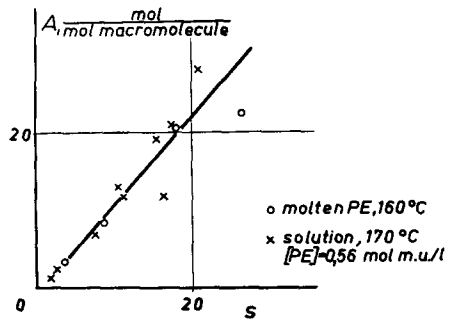
Fig.8. Average number of carboxylic
groups (A) plotted against
the average number of chain
scissions (s)

PE molecules are statistical coils both in solution and in
melt, significant molecular order does not occur. Therefore
steric conditions of initiation, propagation, and termination
of the oxidative chain will mostly be the same. This leads to
similar oxidation mechanisms. However, the analogy of the
overall processes do not mean the identity of the mechanisms in
every details. For example, the differences in the $W_{Z,max}$ vs.
Y_{max} relationship (Table 1) and Y vs. Z curves (Fig.3) refer
to this.

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