Hydroperoxidation in the low-temperature thermooxidation of linear low density polyethylene

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Thermooxidation at 80°C of two types of low density polyethylene (ethylene–1-butene and ethylene–1-propene) was examined from i.r. spectroscopic measurements. The maximum concentration of isolated hydroperoxides was determined and compared with the initial content of vinyl and vinylidene unsaturations of the polymer films.

(Keywords: hydroperoxidation; thermooxidation; LLDPE)

Introduction

Among the different types of functional groups formed during the degradation process of polymers, hydroperoxide species remain the key products for a good understanding of the oxidation mechanism. Details of the structure of these groups can provide useful information regarding the mechanisms and kinetics of polymer degradation. Investigations have been undertaken in our laboratory over the past decade in primary hydroperoxidation of polyolefins[1,2]. Low-temperature thermooxidation (85 or 95°C) of different polyolefins has been examined. The major finding of these studies was that hydroperoxidation observed in the α position of vinylidene species produces isolated hydroperoxide groups that absorb at 3550 cm^{-1} and are stable at 85°C.

Thermooxidation investigations at low temperature on ethylene–α-olefin have been carried out and the hydroperoxide concentration has been determined from *FT*i.r. measurements. This method is the most convenient for the observation of isolated hydroperoxides formed on vinylidene sites. Preliminary results are presented in this paper.

Experimental

Samples: The samples used in this work were kindly supplied by Exxon. Two types of linear low density polyethylene (LLDPE) were used: ethylene–1-butene (EB) and ethylene–1-hexene (EH). They were processed in the form of films 100 μm thick. The initial content of vinyl and vinylidene species was estimated by i.r. spectroscopy on the basis of the molar extinction coefficients as follows:

$$\varepsilon \text{ (vinyl, 909 cm}^{-1}) = (122 \pm 7) \text{ mol}^{-1}\,\text{l cm}^{-1}$$

$$\varepsilon \text{ (vinylidene, 888 cm}^{-1}) = (158 \pm 7) \text{ mol}^{-1}\,\text{l cm}^{-1}$$

$$\varepsilon \text{ (}trans\text{-vinylene, 965 cm}^{-1}) = (100 \pm 10) \text{ mol}^{-1}\,\text{l cm}^{-1}$$

All values recorded are listed in *Table 1*. Other physical data for these samples are also summarized in *Table 1*.

I.r. measurements. I.r. measurements were performed using an *FT*i.r. spectrometer (Nicolet 20 SX).

Results and discussion

During thermooxidation at 80°C, the same changes in the hydroxyl, carbonyl and unsaturation regions were observed for all samples. For a detailed description of these changes see ref. 3. In particular, the formation of isolated hydroperoxides and the gradual disappearance of unsaturation bands in the spectrum of the oxidized sample were monitored. The maximum concentration of isolated hydroperoxides formed in each sample was calculated from the absorbance at 3550 cm^{-1}. All data are collected in *Table 1*.

As in our previous studies, it was found that the concentration of isolated hydroperoxides matches the initial concentration of vinylidene for EH copolymers. That is no longer true for EB copolymers (except EB2), where it equals the amount of initial concentrations of vinyl and vinylidene species. From this result, it seems that the vinyl groups may also be categorized as preferential sites of primary hydroperoxidation, contrary to what has been observed to date. We suspect a mechanism of hydroperoxidation similar to that proposed previously in vinylidene species[1]:

$$\begin{array}{l} CH_2{=}CH{-}CH_2{-} + r^{\bullet} \rightarrow CH_2{=}CH{-}CH^{\bullet} + rH \\ \qquad\qquad\qquad\qquad\qquad\quad \Big\downarrow O_2,\ PH \\ CH_2{=}CH{-}CH{-} + P^{\bullet} \\ \qquad\qquad\quad\ \ | \\ \qquad\qquad\quad\ \ OOH \end{array}$$

The question is why primary hydroperoxidation on vinyl species takes place only in EB copolymer. This observation cannot be attributed to the physical parameters of the samples. No relationship is observed between any of the physical parameters and the reactivity of vinyl species. One may suspect the initial content of

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Table 1 Characteristics of LLDPE films, the initial contents of unsaturations, the sum of vinyl and vinylidene groups, and the maximum concentrations of isolated hydroperoxides formed during the thermooxidation process at 80°C

Sample	Melt index $(g(10\,min)^{-1})$	Density $(g\,cm^{-3})$	Oxygen permeability $(l\,m^{-2}\,atm^{-1}\,(24\,h)^{-1})$	Initial content of vinyls $(mol\,l^{-1} \times 10^3)$	Initial content of vinylidenes $(mol\,l^{-1} \times 10^3)$	Sum of the initial contents of vinyls and vinylidenes $(mol\,l^{-1} \times 10^3)$	Concentration of isolated hydroperoxides $(mol\,l^{-1} \times 10^3)$
EB1	1	0.918	1.2 ± 0.1	7.8	2.7	10.5	11
EB2	0.7	0.925	0.84 ± 0.01	11	4.2	15	4.4
EB4	2.8	0.918	1.16 ± 0.05	8.9	4.9	13.8	17
EB5	1	0.935	0.52 ± 0.02	4	2.7	6.7	5.5
EH1	2.8	0.917	1.05 ± 0.15	19.5	14	33.5	13
EH2	0.8	0.921	1.26 ± 0.09	16	13	29	15
EH3	0.8	0.926	0.77 ± 0.03	15	8.5	23.5	6.6
EH4	1.8	0.920	1.2 ± 0.1	17	16	33	15

the branch point (which we did not assess here), but our previous study showed that the maximum intensity of the 3550 cm^{-1} band is not related to it[1]. The explanation probably lies in the type of α-olefin used to process the film. This interpretation confirms our previous study on the importance of α-olefin in the general mechanism of oxidation[4].

It is worth mentioning, in both types of copolymer, the non-participation of *trans*-vinylene groups in the formation of isolated hydroperoxides.

Obviously, extensive additional work on several types of polyolefins is required to confirm our observations.

References

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