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Original Scientific Paper

The Effect of Ferrocene Derivatives on the Thermal Degradation of Polyethylene*

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The inhibiting action of ferrocene and *p*-ferrocenyl-aniline on the kinetics of thermal degradation of polyethylene was investigated by gravimetry, by measuring the changes in average molecular weight, by gas chromatography and spectroscopic techniques. The effect of ferrocene derivatives is explained by assuming chemical reactions of the decomposition products (such as cyclopentadiene and cyclopentadienyl radicals) with macroradicals to occur.

One of the methods for increasing the thermostability of polyolefins is the application of stabilizers capable of reacting with alkyl macroradicals and, consequently, of terminating polymer degradation chains at high temperatures (300—400 °C). Metalloorganic compounds, in particular ferrocene derivatives, seem to be very promising in this respect. Successful use of these compounds as antirads and antioxidants for some polymers (polyvinyl alcohol, elastomers, polyethylene) has been reported[1].

The inhibiting action of ferrocenes is usually ascribed to their »aromatic« nature and their capability of electrophilic substitution[2]. However, this concept has not been confirmed experimentally.

This research was conducted in order to test the possibility of applying ferrocene derivatives as thermostabilizers against degradation of polyethylene, and to obtain some insight into the mechanism of such action.

EXPERIMENTAL

Materials

Use was made of low-density (high-pressure) commercial polyethylene, of ferrocene and *p*-ferrocenylaniline. Their characteristics were as follows:

Polyethylene (PE): $\overline{M}_w = 3 \cdot 10^4$, m. p. 110 °C, $CH_3/1000\ C = 21.4$, $-CH = CH_2/1000\ C = 0.16$ (by i. r. spectroscopy); peroxy groups were absent (by iodometry).

Ferrocene (Fc) and *p*-ferrocenylaniline (FcAn) were prepared by routine techniques[2]: Fc — mol. wt. 188, m. p. 174 °C, stable up to 400 °C; *p*-FcAn — mol. wt. 279, m. p. 157—159 °C; both soluble in alcohols, acetone, ethylene dichloride, benzene.

The additives, dissolved in absolute ethanol, were introduced into the powdered polymer by thorough mixing in an agate pestle and subsequent drying *in vacuo*. The colour of the polymer became faintly orange.

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* Based upon the lecture delivered to the First Yugoslav Symposium on polymer degradation and stabilization, 13—16. 3. 1974.

Methods

The effect of additives on the kinetics of thermal degradation was investigated in vacuo ($p = 10^{-4}$ Torr) at temperatures of 300—400 °C, in ampoules having a sealed trap for freezing the gaseous degradation products.

The degradation kinetics was studied gravimetrically, as well as investigating the variations in molecular weight, the accumulation of hydrocarbon gases ($C_1 — C_4$), and the functionality of polymer fragments.

Gravimetric measurements were made, as usual, by determining the loss of weight of polymer samples: $a = (g_o - g_t)/g_o$ is the degree of degradation, where g_o is the initial weight of the sample (usually about 20 to 40 mg $[(0.7 - 1.4) \cdot 10^{-3}$ mol $C_2H_4])$, while g_t denotes the weight of the sample after degradation time t.

The molecular weights were determined by viscosimetry in decaline at $T = 135\ ^0C$ ($[\eta] = 4.6 \cdot 10^{-4}\ \overline{M}_v^{0.73})^3$. In the case of our polymer $\overline{M}_v \approx 1.05\ \overline{M}_n$.

The number of polymer chain scissions, n, in the time t after the beginning of degradation was calculated from the expression:

$$n = M_o \left(\frac{1 - a}{\overline{P}_{nt}} - \frac{1}{\overline{P}_{no}} \right),$$

where M_o is the amount of polymer, $a = \Delta g/go$ is the degree of degradation, and $\overline{P}_{no}$ and $\overline{P}_{nt}$ are mean numerical values of the polymerization degree for the initial and degraded polymer, respectively.

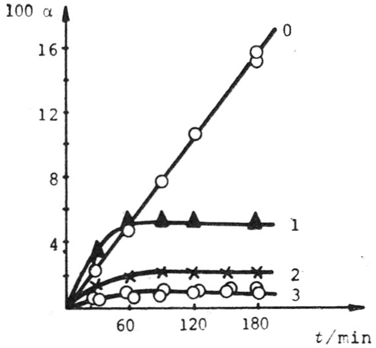
Gas chromatography was used for the identification of gaseous hydrocarbons. We used a Pye-Unicam Panchromatograph with glass column $l = 2$ m, $d = 6$ mm, packed with silicagel. The column temperature was 50—75 °C, and a thermal conductivity detector, with He as the carrier gas (50 ml/min) were used.

The solid residues were analysed by infra-red spectroscopy for the presence of $—CH_3$, $—CH{=}CH_2$, $—CH{=}CH—$ and other functional groups. The i. r. analysis was made by means of Hitachi Epi-S2 and UR-10 instruments. The samples were in the form of polymer films (thickness $\leqslant 5 \cdot 10^{-2}$ mm), or KBr pellets.

The inhibitor conversion in the course of polyethylene degradation was followed by means of i. r. and γ-resonance (Mössbauer) spectroscopy.[4] The Mössbauer spectrometer was of the electrodynamic type with constant acceleration, ^{57}Co in Cr source Plane-parallel cells were used for γ-resonance measurements.

RESULTS AND DISCUSSION

Both Fc and p-FcAn markedly inhibited the thermal degradation of polyethylene over the temperature range studied. The optimum additive concentration was 0.5% by weight of polymer. However, ferrocene was more effective than its derivative, as can be seen in Figs. 1 and 2, curves 1 and 2 for $T = 350\ ^0C$. There are two stages of polymer degradation in the presence of inhibitors. At the initial stage ($t \leq 1$ hour) some difference in Fc and p-FcAn action was observed. In the presence of p-FcAn some acceleration of weight loss takes place, and molecular weight decreases as compared with polymer sample without additions (Figs. 1 and 2, curves 0 and 1). Ferrocene had no influence on the rate of the molecular weight decrease (Fig. 2, curves 0 and 2) and a weak influence on the loss of weight (Fig. 1, curves 0, 2). After this initial stage (on the second stage) of degradation the inhibiting action of both additives became more effective. After 1 hour of exposure the weight loss and evolution of volatiles becomes very low, or stop completely (Fig. 1 and 3). At the same time there is no further decrease of molecular weight, but some tendency for increase appears (Fig. 2, curves 1 and 2), which seems to be due to cross-linking.



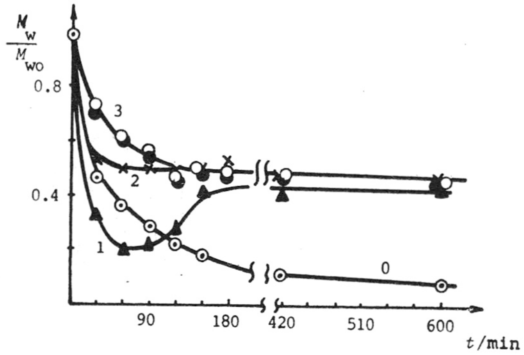


Fig. 1. The kinetic of thermal degradation of low-density polyethylene in the presence of difference inhibitors (gravimetric). $T = 350$ °C. Curves: 0 — without inhibitor; 1 — 0.5% by wt. p-FcAn; 2 — 0.5% by wt. Fc; 3 — 0.3% cyclopentadiene (CPD, ○); — 0.3% cyclohexadiene (CHD, ●).

Fig. 2. Variations in molecular weight (M_v/M_{n_0}) of polyethylene on thermal degradation in the presence of various additives. $T = 350$ °C. Curves: 0 — without inhibitor; 1 — 0.5% by wt. p-FcAn; 2 — 0.5% by wt. Fc; 3 — 0.3% by wt. CPD (○); — 0.3% by wt. CHD (●).

The regularity of the variation of chain-cleavage numbers (n) is complex, especially in the presence of p-FcAn (Fig. 4, curve 1 with clear maximum).

The difference in Fc and p-FcAn effects at the initial stage of degradation can be ascribed to the appearance of aniline radicals capable of abstracting H atoms from macromolecules, with consequent initiation of new kinetic chains.

It is displayed in the increase of the chain-cleavage and loss of weight rates (Fig. 4 and 1, curves 1). As a result we observed also a deep minimum on the curve 1, Fig. 2 at expositions near 1 hour as compared with PE without additives (curve 0).

Analysis of the γ-resonance spectra of polyethylene pyrolyzed in the presence of p-FcAn showed that the inhibitor actually decomposed (Fig. 5). A new line ($S_1 = 0.4$ mm/s isomer shift, $\Delta_1 = 0.0$ quadrupole splitting) appeared in the γ-resonance spectrum of the specimen heated at 350 °C, in addition to

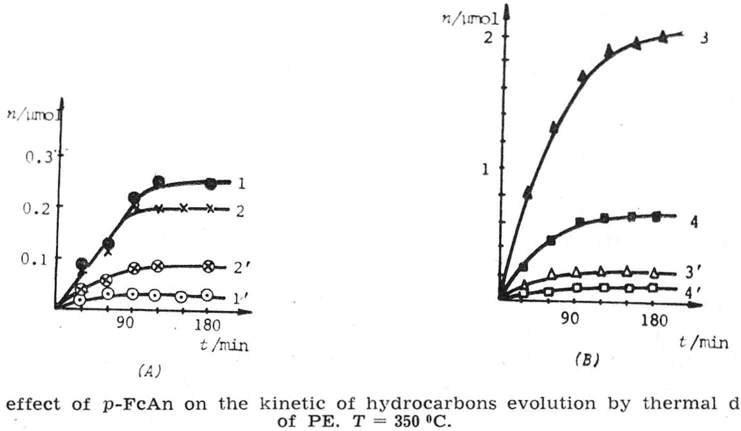


Fig. 3. The effect of p-FcAn on the kinetic of hydrocarbons evolution by thermal degradation of PE. $T = 350$ °C.

a) ethane 1,1′; ethylene 2,2′;
b) propane 3,3′; propylene 4,4′.
1—4 — without inhibitor; 1′—4′ — 0.5% by wt. p-FcAn.

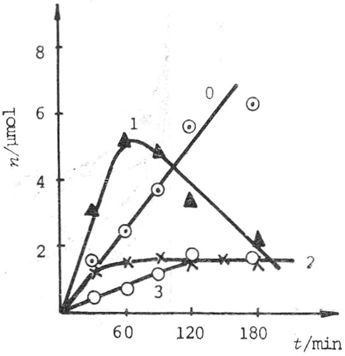


Fig. 4. The kinetics of the chain cleavage of polyethylene macromolecules on thermal degradation in the presence of various additives. n — number of chain scissions in polymer sample ($1.4 \cdot 10^{-3}$ mol C_2H_4). $T = 350$ °C.
Curves: 0 — without inhibitor; 1 — 0.5% by wt. p-FcAn; 2 — 0.5% by wt. Fc; 3 — 0.3% by wt. CPD.

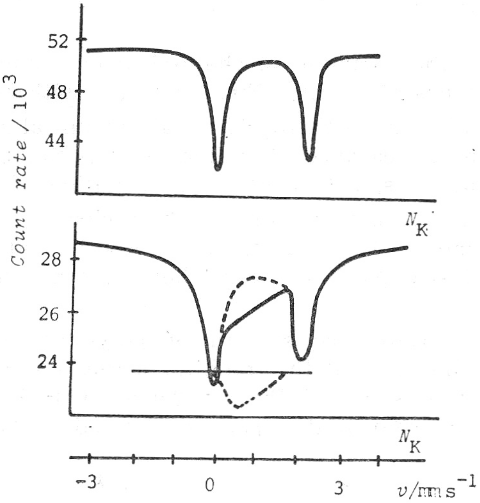


Fig. 5. γ-resonance spectrum of p-FcAn in polyethylene under different conditions of thermal treatment:

(a) p-FcAn in polyethylene before heating ($T = 25$ °C);
(b) the same after melting in vacuo ($T = 120$ °C);
(c) the same after polymer degradation in vacuo at $T = 350$ °C, exposure for 1 hr.

the line $S_0 = 0.8$ mm/s and $\Delta_0 = 2.24$, exhibited by initial p-FcAn. It was ascribed to non-ferromagnetic fine disperse iron[5] formed in the cracking of FcAn.

The fraction of decomposed inhibitors did not exceed 15% of its initial concentration. In this case other fragments of the ferrocene structure: cyclopentadiene and cyclopentadienyl radicals had to be present in the system. These compounds have been observed in the products of ferrocene pyrolysis at 500—520 °C[6,7]. The decrease in the inhibitor decomposition temperature by 100—150 °C seems to be accounted for by the action of polyethylene macroradicals formed at the initial stage of degradation.

The conclusion was made that the inhibiting action of ferrocene and its derivatives was due to cyclopentadiene and cyclopentadienyl. This was confirmed by experiments on the direct effect of cyclodienes CPD, CHD (cyclopenta- and hexadienes) on the thermal degradation of polyethylene (Figs. 1, 2, and 4 curve 3)*. In this case the inhibitors came into play at the start of polymer degradation and their efficiency was higher than that of ferrocene (at a concentration of 0.2—0.3 per cent by weight).

As can be seen from Figs. 1, 2 and 4, curve 3, cyclopentadiene markedly reduced the rate of weight loss, the rate of molecular weight decrease of PE and the number of chain scissions already at the initial stage of degradation, as compared with ferrocene compounds. At the second stage the presence of monomer dienes completely prevented the chain-cleavage of macromolecules as well as the weight-loss. The same effect was observed also in the case of CHD.

The length of polymer fragments after degradation was 0.5 of the initial one and was maintained for 10—12 hours at 350 °C (Fig. 2).

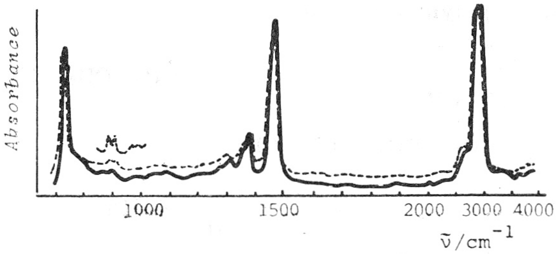
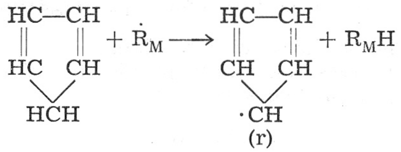


Fig. 6. I.r. spectrum of polyethylene degradation products in the presence of cyclopentadiene, $T = 350$ °C, exposure for 1 hr; (—) before; — — after degradation.

I. r. analysis of degradation products in the presence of cyclodiene made evident the chemical interaction between inhibitor and polymer (Fig. 6) (appearance of 895 cm^{-1} bands from conjugated and 965—980 cm^{-1} bands from unconjugated —C=C— double bonds in closed cycle).

The following mechanism of inhibition was postulated on the ground of these results. Owing to the high mobility of the H atom in the CH_2 group of cyclodiene it is readily abstracted by macroradicals:



(1)

The cyclodienyl radicals, being of an allyl type, are inactive (or low active) and can not propagate kinetic chains, *i. e.* reaction (1) terminates the kinetic chains of polymer degradation and must inhibit chain scissions.

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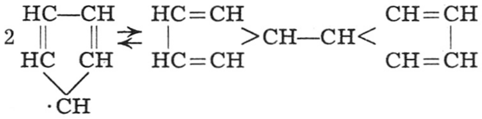
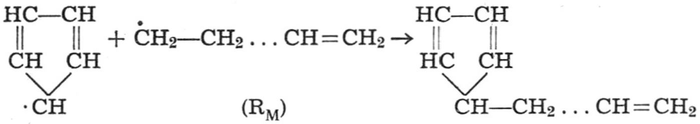
* The reaction mixture was in closed ampoules in order to prevent volatilization of cyclodienes.

Radicals $\dot{r}$ can disappear either by recombination



(2)

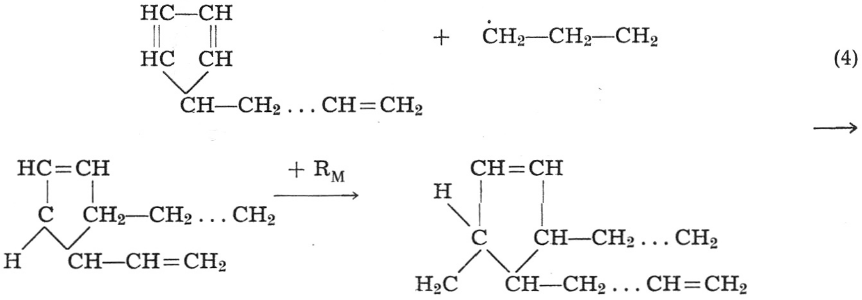
or by interaction with macroradicals



(3)

Reaction (3) seems to be predominant at high temperatures, since the dimer (dicyclopentadiene) is unstable and its decomposition regenerates two $\dot{r}$ radicals.

The products of reaction (3) can interact with macroradicals (R_M) at the double bonds in cycle, which is in accordance with the observed increases of molecular weights of polymer residues:



(4)

The low solubility of polymer residues at high inhibitor concentrations seems to be connected just with reaction (4).

CONCLUSION

The inhibiting effect of ferrocene seems to be accounted for by the participation of its decomposition products in the steps of depropagation of kinetic chains. It consists in the replacement of alkyl macroradicals by conjugated allyl radicals which are inactive in kinetic chain propagation.

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SAŽETAK

Učinak derivata ferocena na toplinsku razgradnju polietilena

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Proučavano je inhibitorno djelovanje ferocena i p-ferocenilanilina na toplinsku razgradnju polietilena. Kinetika razgradnje slijedila se gravimetrijski, zatim mjerenjem u prosječnoj molekularnoj težini, te plinskom kromatografijom i spektroskopskim tehnikama. Učinak derivata ferocena objašnjen je pretpostavljajući rekcije razgradnih produkata (ciklopentadien i ciklopentadienil-radikali) s makroradikalima, što je i potvrđeno u zasebnim pokusima.

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