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FORMATION OF INHIBITOR RADICALS DURING THE OXIDATION OF POLYPROPYLENE

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To elucidate the mechanism of action of inhibitors in chain degenerate-branched oxidation processes, the greatest interest lies in studying the intermediate stages, their chemistry, and their rates. The only attempt to approach the solution of this problem from such a standpoint was made by Charles and Thomas (^{1}), who investigated the change in radical concentration during the oxidation of hexadecane at 170° in the presence of phenyl-β-naphthylamine as inhibitor. The authors were unable to reach an unambiguous conclusion about the chemistry of the intermediate stages, since the structure of the radicals was not identified. Moreover, radicals could not be detected during the oxidation of hexadecane in the presence of other inhibitors. Thus, this attempt cannot be considered successful.

By the method of electron paramagnetic resonance (EPR), we investigated the structure and kinetics of accumulation of radicals formed during the oxidation of isotactic polypropylene in the presence of a number of typical inhibitors. The oxidation was carried out in glass ampoules placed directly in the resonator of an EPR-2 spectrometer (^{2}) and blown with a stream of hot air. The constancy of the jet temperature was maintained by an electronic thermoregulator, with a platinum bolometer serving as the sensor. The temperature accuracy was 0.5°–1.0° in the range 20–250°. At the same time as the EPR signals were recorded, it was possible to take readings from a manometer connected to the ampoule and to follow the rate of oxygen uptake. Polypropylene films were obtained by pressing a powder into which an alcoholic solution of the inhibitor had first been introduced with thorough mixing, after which the alcohol was pumped off in vacuum. The thickness of the films did not exceed 100 μ. Pieces of film of definite weight were placed in the ampoule so that they only covered the inner surface of that part of the ampoule which is located in the resonator. Under these conditions oxygen diffusion does not limit the oxidation rate, and a kinetic structural formulas of binaphthol (I) and octyl-4-methylphenol (II)

Figure 1: structural formulas of binaphthol (I) and octyl-4-methylphenol (II)

Fig. 1. EPR spectra of radicals: a—α-naphthol; b—β-naphthol; c—binaphthol; d—phenol

Figure 2: Fig. 1. EPR spectra of radicals: a—α-naphthol; b—β-naphthol; c—binaphthol; d—phenol

regime is well satisfied. The concentration of inhibitor in the film was $7 \cdot 10^{-2}$–$9 \cdot 10^{-2}$ mol/kg.

As inhibitors we used typical representatives of various classes of inhibitors: α- and β-naphthols, binaphthol (I), 2,6-ditertiary-

octyl-4-methylphenol (II), and diphenylamine. The EPR spectra of the radicals of these inhibitors are shown in Figs. 1 and 2. Such radicals are obtained in reac-

of inhibitors with peroxy radicals under conditions modeling the oxidative process (metal-salt-catalyzed decomposition of hydroperoxides in hydrocarbon solutions) ([3], [4]). The radicals of α- and β-naphthols are characterized by singlet spectra (Fig. 1 *a, b*) with widths between the points of maximum slope of 3 and 5 oersted, respectively; they are probably formed by abstraction of hydroxyl hydrogen and are stabilized by strong conjugation of the unpaired electron with the system of π-bonds of the naphthyl rings, the magnitude of this conjugation in the α-naphthoxyl radical being greater than in β-naphthoxyl, which also corresponds to their relative kinetic stability.

Fig. 1. EPR spectra of radicals: *a*—α-naphthol; *b*—β-naphthol; *c*—binaphthol; *d*—phenol.

Radicals from binaphthol (I) and phenol (II), having their own characteristic EPR spectra, are obtained in the same way. In both cases, upon reaction with peroxy radicals, abstraction of hydroxyl hydrogen occurs; in binaphthol the unpaired electron interacts strongly only with two equivalent protons of the naphthyl rings, which leads to the appearance of a triplet (Fig. 1*c*), whereas in the phenoxyl radical the strong interaction of the unpaired electron with the protons of the methyl group located in the para position to the oxygen atom gives the principal quartet, each component of which is split into three lines owing to interaction with the meta protons (Fig. 1*d*).

In the reaction of diphenylamine with peroxy radicals, diphenyl nitroxide is obtained; the mechanism of its formation can be represented as the sequence of two reactions:

$$\mathrm{Ph_2NH} + \dot{\mathrm{R}}\mathrm{O_2} \rightarrow \mathrm{Ph_2}\dot{\mathrm{N}} + \mathrm{ROOH};$$

Fig. 2. EPR spectra of diphenyl nitric oxide radicals in concentrated toluene solution

Figure 3: Fig. 2. EPR spectra of diphenyl nitric oxide radicals in concentrated toluene solution

$$\mathrm{Ph_2\dot{N} + \dot{R}O_2 \rightarrow Ph_2\dot{N}O + \dot{R}O.}$$

The EPR spectrum of diphenyl nitroxide (Fig. 2) is a triplet with an equal ratio of component intensities and a splitting of 10.3 oersted, arising from interaction of the unpaired electron with the nucleus of N^{14}. Each component of the triplet is split into 15 lines owing to interaction with the ortho- and para-proton groups of the benzene rings. At high dilution, because of further removal of exchange interaction, a hyperfine structure associated with the meta protons appears.

The radicals formed during oxidation of polypropylene in the presence of the above-mentioned inhibitors give EPR spectra exactly corresponding to the spectra of the radicals of the same inhibitors obtained in model-

conditions. This proves the identity of the structure of the radicals and the identity of the mechanisms of their formation in both cases.

Figure 3a shows how the concentration of α-naphthol radicals (number of radicals per gram of polypropylene) changes during oxidation of the film (curve 1). Curve 2 illustrates oxygen absorption (change in pressure in mm Hg) during oxidation at 200°. The initial segment of curve 1 is autocatalytic in character, i.e., at first the rate of radical formation is small, then it gradually increases and reaches a maximum. Subsequently, as the inhibitor is consumed, the radical concentration falls, since the rate of their disappearance exceeds the rate of formation. After this, oxygen absorption begins and the reaction leaves the induction period. The curve of change in radical concentration reflects the chain, degenerately branched process that occurs during oxidation. Curves $1'$ and $2'$ correspond to oxidation of polypropylene powder under otherwise identical conditions. From these curves it follows that the induction period of powder oxidation is greatly reduced, and the maximum radical concentration drops sharply in comparison with the same quantities during oxidation of the film. Hence an important conclusion follows concerning the dependence of the effectiveness of an inhibitor on the method of introducing it into the polymer, which determines the character of the inhibitor distribution. Pressing polypropylene powder (at 120°, in a CO_2 atmosphere, at a pressure of 150 $\mathrm{kg/cm^2}$) promotes homogeneous distribution of the inhibitor throughout the entire mass of the polymer, whereas in the powder the inhibitor is adsorbed only on the surfaces of the polymer grains, which reduces its effectiveness.

Fig. 2. EPR spectra of diphenyl nitric oxide radicals in concentrated toluene solution

Fig. 3. Change in concentration of inhibitor radicals and oxygen absorption during oxidation of polypropylene film

Figure 4: Fig. 3. Change in concentration of inhibitor radicals and oxygen absorption during oxidation of polypropylene film

The same regularities are observed during oxidation of a polypropylene film with α-naphthol at 220° (the concentration of α-naphthol is the same as in the preceding— in the latter case, was $7 \cdot 10^{-2}$ mole/kg) (Fig. 3b). The induction period decreases with increasing temperature, while the maximum concentration of radicals increases somewhat. β-Naphthol behaves similarly (Fig. 3c). The character of the curves remains the same as in the presence of α-naphthol; however, the induction period is almost half as long, and the maximum concentration of β-naphthol radicals is almost an order of magnitude lower than in the case of α-naphthol under the same conditions, which is consistent with the considerably lower kinetic stability of β-naphthol radicals and the higher rate of their decay compared with α-naphthol radicals. The kinetic curves we obtained for the accumulation and consumption of inhibitor radicals and the curves of oxygen absorption during the oxidation of polypropylene films in the presence of phenol (II) (at its concentration of $7 \cdot 10^{-2}$ mole/kg) and diphenylamine ($9 \cdot 10^{-2}$ mole/kg) show that, for both inhibitors, shorter induction periods and low radical concentrations at the maximum are characteristic; however, the form of the curves does not change substantially. Binaphthol (I), as an inhibitor in the oxidation of polypropylene in film, behaves analogously.

Fig. 3. Change in the concentration of inhibitor radicals (1) and oxygen absorption (2) during oxidation of polypropylene film. **a**—α-naphthol, 200°; **b**—α-naphthol, 220°; **c**—β-naphthol, 200°. Inhibitor concentration $7 \cdot 10^{-2}$ mol/kg, oxygen pressure 400 mm Hg. Curves $1'$ and $2'$ refer to oxidation of polypropylene powder in the presence of α-naphthol ($7 \cdot 10^{-2}$ mol/kg, 200°, 400 mm Hg).

The character of the curves for the accumulation and consumption of inhibitor radicals indicates that most of the radicals are formed as a result of the termination of the kinetic oxidation chains, which is a complex chain process with pronounced branching.

The application of M. B. Neiman’ s kinetic isotope method, extended to radicals labeled with isotopic nuclei having different magnetic moments and giving characteristic EPR spectra, will make it possible to determine the rates of formation and consumption of radicals. With simultaneous study of the kinetics of inhibitor consumption and oxygen absorption, this provides an opportunity to approach a quantitative solution of the problem.

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