

THERMAL OXIDATION OF PROPYLENE/STYRENE COPOLYMERS. IR SPECTROSCOPIC STUDIES

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Summary

It can be summarized that all of the units or segments of the copolymers are involved in the degradation. The macromolecules undergo quite essential changes. As a consequence of oxidation, various oxygenated groups such as peroxides, hydroperoxides, lactones, esters, ketones, carboxylic acids are formed in the copolymers. The order of their concentration is as follows:

lactones < esters < acids, ketones < peroxides

The sequence of susceptibility of the individual hydrocarbon groups of the macromolecule to oxidation is the following:

hydrocarbon groups in the main chain of the macromolecule >
> aromatic side-groups >
> CH₃ side groups >
> longer isotactic blocks >
> shorter isotactic blocks.

Introduction

Susceptibility of a polymer to oxidation is influenced by several factors. Possibly, the most important one is the structure of the macromolecule. Saturated unbranched polymers are hardly oxidable. With increasing concentration of branches, oxidation capability of polymers is growing markedly but the presence of methyl or phenyl groups may protect the polymer chain against the effect of oxygen [1-3].

Polypropylene is known to have good physico-mechanical properties and easy processability. The tertiary hydrocarbon sites in the polymer chain are, however, the attackable points of the macromolecule. Polypropylene is, therefore, highly susceptible to oxidation [4, 5].

Very favourable preconditions for peroxide formation are present in polypropylene since the tertiary hydrocarbon bond is weaker than the secondary one by eleven times (the latter is four times weaker than the primary one) [6]. Consequently, the great majority of the appeared peroxide and hydroperoxide radicals is resulted from the interactions with tertiary

hydrocarbons [7–8]. Decomposition rate of a hydroperoxide depends on the polymeric structure [9–10].

Since polypropylene has a high degree of steric order, relatively stable hydroperoxide aggregates can be formed creating favourable conditions for a bimolecular decomposition.

Very few informations have been reported about the kinetic analysis of oxidation of polyolefins. They generally give the simplified kinetic pattern of autoxidation [11–14]. It is especially true in the case of copolymers of olefins with vinyl monomers.

Discussion

Oxidation of propylene/styrene copolymers was carried out in a closed system under oxygen atmosphere at a constant pressure between 160 and 190 °C. Copolymers to be subjected to thermal oxidation contained 8 or 15% of styrene.

Changes in concentrations of oxygenated groups during the reaction were estimated by the absorbance values of bands at 3450, 1775, 1743, and 1720 cm^{-1} .

Since the specific absorbances of the particular species were unknown, only relative changes in the concentrations could be determined. Absorbance ratios of bands at 998 cm^{-1} to 973 cm^{-1} served as internal standards since they were invariant with respect to the molecular composition and to the reaction temperature.

On the basis of the relative changes in concentrations of various carbonyl groups (1775, 1743, 1720–15 cm^{-1}), it can be demonstrated that, up to the oxygen consumption of 2.0 to 2.7 cm^3/g polymer, growing the given groups proceeds at a considerably higher rate than beyond this oxygen consumption when the rates of increase in carbonyl concentrations are reduced. The overall dependence of the carbonyl concentrations on the amount of absorbed oxygen is exponential.

Very weak if any dependence of changes in concentrations of carbonyl groups was observed on the composition of the macromolecule and on the reaction temperature.

Changes in concentrations of OH groups formed through decomposition of hydroperoxide or peroxide compounds show a reversed pattern. Changes were quantified by following the intensity of band at 3450 cm^{-1} (Fig. 1). In the initial stage of the reaction, up to oxygen consumption of 2–3 cm^3 , enrichment of the polymer in OH groups is relatively slow. In the posterior phases of the reaction, however, formation of OH groups accelerates. Similarly to the carbonyl groups, no dependence on the molecular composition and on the temperature could be detected within the studied range.

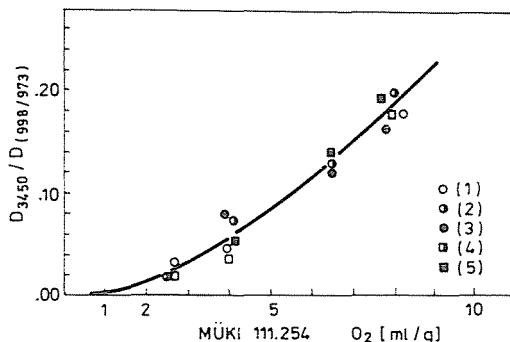


Fig. 1. Changes in concentrations of OH groups

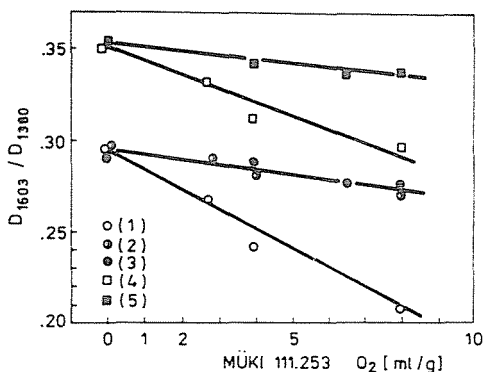


Fig. 2. Changes in absorbance ratio of D_{1603}/D_{1380}

As it is demonstrated below, IR-spectroscopic studies led to the conclusion that every sequential unit of the macromolecule degraded due to oxidation of the copolymer regardless on whether they were propylene or styrene units. During the oxidation of copolymer containing 85% of propylene, absorbance ratio of D_{1603}/D_{1380} decreased from 0.35 to 0.30. It certainly referred to the easier degradation of the styrenic side-groups than the propylenic ones in the macromolecule. Similar observations were found with copolymers of higher propylene content (92%) as well. By elevating the reaction temperature, the different relative susceptibilities of these two kinds of groups to oxidation were equalizing (Fig. 2).

It can be deduced from the absorbance ratio changes in D_{1603}/D_{973} that CH sites in the propylene sequences of the main chain are weaker than those at the styrenic side-groups (Fig. 3). In the course of the reaction, values of the ratio D_{1603}/D_{973} increase. This increase is getting more emphasized by enhancing

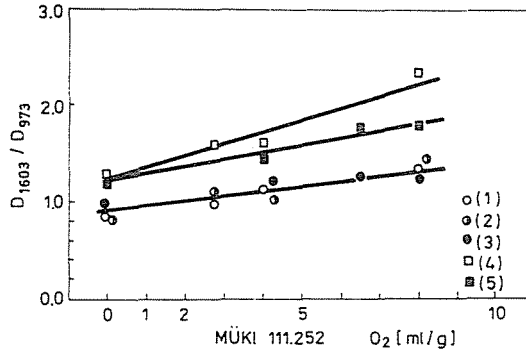


Fig. 3. Relative changes in concentrations of propylenic CH and styrenic side groups

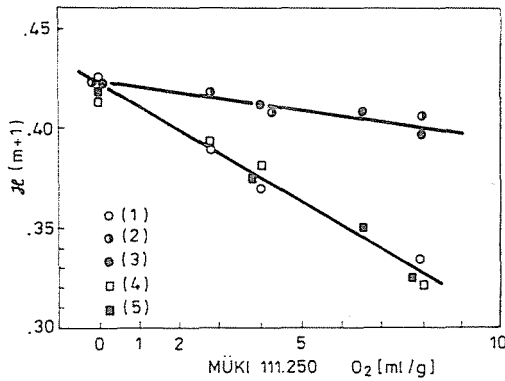


Fig. 4. Changes in absorbance ratio of D_{565}/D_{1603}

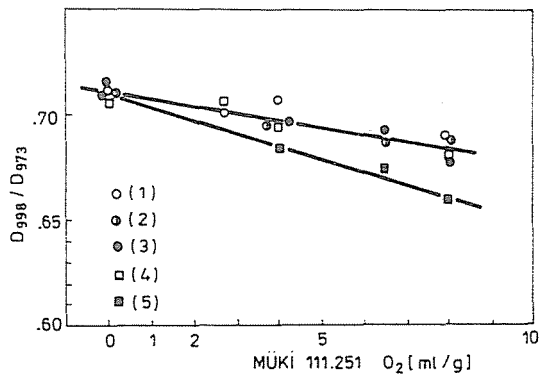


Fig. 5. Degree of steric order of propylene

the concentration of the vinyl comonomer. At low vinyl monomer content (8%), no temperature dependence of this absorbance ratio was observed. At a higher styrene concentration (15%), the extent of changes in the absorbance ratio D_{1603}/D_{973} was reduced with increasing reaction temperature (from 170 to 190 °C). During the oxidation, intensity of band at 565 cm^{-1} changed more markedly than that at 1603 cm^{-1} , i.e. the absorbance ratio D_{565}/D_{1603} dropped from 0.72 to 0.54 as the amount of absorbed oxygen was increasing. Consequently, oxidation takes place even in the longer isotactic blocks of styrene sequences. In fact, styrenic CH sequences in the main chain underwent higher extent of oxidation than the aromatic side-groups of the styrene (Fig. 4).

At higher styrene content (18%), oxidation susceptibility of the two groups is not balancing by raising the reaction temperature. At the same time, at lower concentration of the vinyl comonomer (8%), the difference between the aliphatic and the aromatic groups in the extent of oxidation was reduced with increasing temperature.

As it was mentioned above, the absorbance ratio D_{998}/D_{973} remained practically constant as the reaction was proceeding (Fig. 5). Even in the case of a considerable degradation of the molecule, this ratio was diminished slightly: from 7.1 to 6.9 or 6.8. At higher styrene content (15%) at a higher temperature (190 °C), reduction in absorbance ratio D_{998}/D_{973} was still more emphasized a bit but the experimental data led to the conclusion that the degree of steric order of propylene units was not subjected to any changes.

Absolute concentration of CH_3 groups changed only slightly during the oxidation of the copolymer. In copolymers of low styrene content (8%), frequency of CH_3 groups in term of 100 carbon atoms reduced from 45/100 to 44–41/100 during the oxidation reaction. In copolymers of higher styrene content, decrease in occurrence of CH_3 groups was somewhat more considerable with increasing reaction time (from 44/100 to 37/100) (Fig. 6).

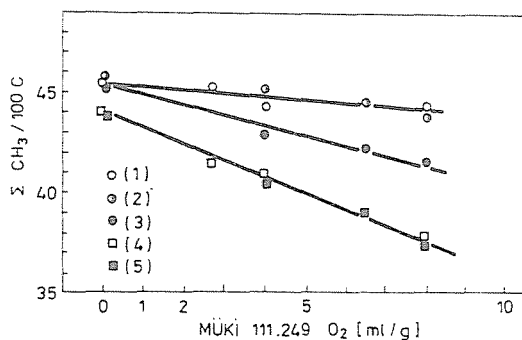


Fig. 6. $\text{CH}_3/100\text{ C}$

Conclusion

It can be concluded from the discussion of experimental data that, in propylene/styrene copolymers, relative concentration of CH groups belonging to propylene decreases more rapidly than those of styrene units, i.e. relative susceptibility of the former to oxidation is higher than that of the latter. This difference on oxidation susceptibility is growing with increasing styrene content of the copolymer while it is decreasing with rising temperature.

Degree of crystallinity of copolymers is moderately reduced with the increasing amount of consumed oxygen. A rise in reaction temperature by 10–20 °C results in a more emphasized still not considerable drop in the degree of crystallinity.

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