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Weakened bonds in polymer degradation intermediates as probable sites of macromolecular scission

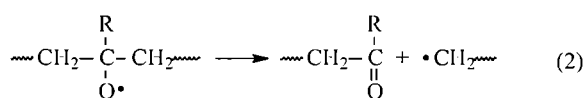
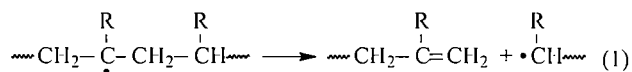
RAPID COMMUNICATION

Summary — Bond strengths in macroradicals and hydroperoxides of polypropylene and polystyrene have been estimated using quantum chemical methods. Both secondary and tertiary polypropylene oxy macroradicals have been found to be clearly inclined to β -scission of main chains. Bond strengths in the main chain of polystyrene alkyl macroradicals proved to be almost unchanged in comparison with initial macromolecule. Among oxygen-containing polystyrene intermediates the most degradable ones seem to be secondary oxy and secondary peroxy macroradicals.

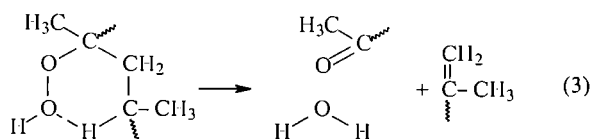
Key words: photooxidation, macromolecular scission, quantum chemical method, polypropylene, polystyrene.

POLYMER DEGRADATION MECHANISM

Investigations on polymer degradation and stabilization are of a continuous interest due to their great practical importance [1–7]. The main cause of polymer properties deterioration is recognized to be macromolecular scission reactions intermediated with oxygen-containing radicals [1, 2]. There are several points of view on what reactions and species play the most important role in the chain scission process. It is generally agreed that the principal mode of main chain scission is decomposition of macroradicals (so called β -scission) [2]:

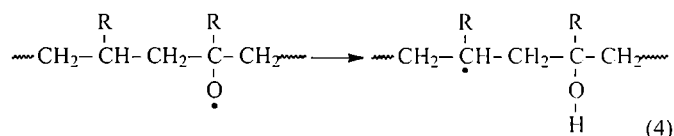


One more pathway to main chain scission may be an intramolecular decomposition of tertiary hydroperoxides in polypropylene [2]:



Meantime, the recent paper [3] warns against overestimation of β -scission reaction of alkoxy radicals [equation (2)]. The referred experimental data on low-molecu-

lar model alkoxy radicals indicate a quite great probability of rearrangement (isomerization) reactions:



An experimental estimation of dominating pathways in real polymer is quite complicated considering that all of the intermediates are highly reactive species which are present in very low concentrations. Besides, very short life times prohibit their extensive analysis. On the other hand some additional information on polymer degradation mechanism may be obtained using quantum chemistry methods, which result in quantitative parameters of molecular structure [8].

Quantum chemistry approaches are frequently used for comprehension of chemical phenomena due to quite reliable evaluation of spatial structures and energies of chemical species as well as electron-shell characteristics. The most straight methods are of course the *ab initio* ones based directly on numerical solution of Schrödinger equation. At the same time, in order to make the calcula-

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tions feasible many simplifications are imposed even for small molecules. In one's turn, long polymer chains are not treatable directly *via ab initio* methods except for short model compounds. For that reason some simplified approaches allow for at least a qualitative insight towards understanding polymer degradation mechanisms. Semi-empirical quantum chemistry methods along with natural bond orbital (NBO) analysis [9] seem to be promising tools for this purpose providing valuable information about molecular parameters.

To estimate possible pathways of macromolecule backbone scission the reasonable parameters may be the bond order and the bond length indicating weakened chemical bonds and suggesting inferences about susceptibility of a polymer chain to scission reactions. In the present paper the above mentioned structural parameters have been estimated basing on semi-empirical approach and they have been related to probable mechanism of polystyrene and polypropylene degradation.

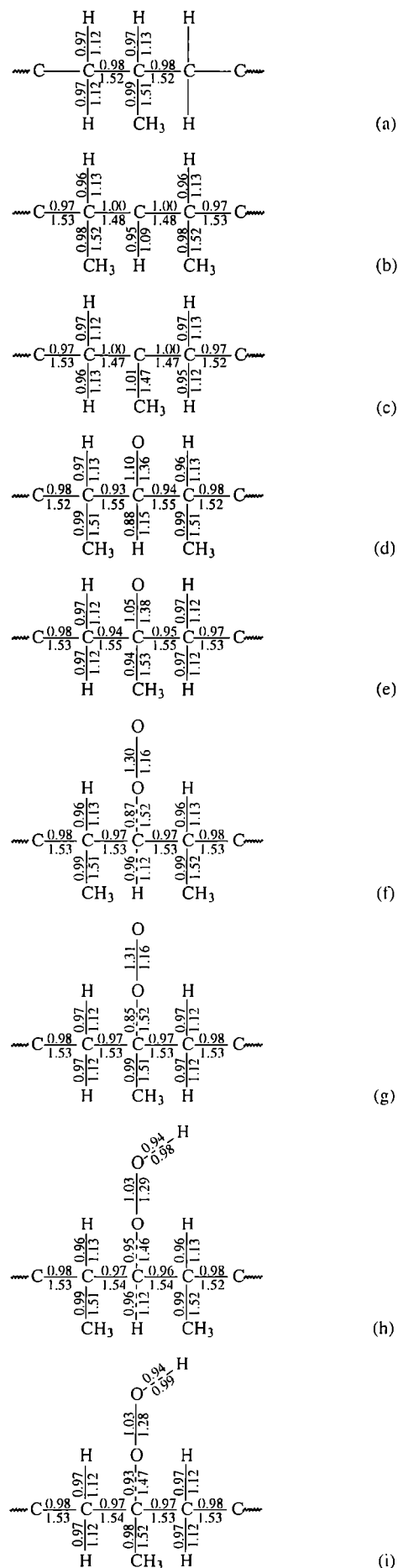
MODELS AND METHODS

The model polymer chains were composed of 35 monomer units of oligopropylene and of 30 of oligostyrene. The data presented relate to a central unit. Initial structures of macromolecules, macroradicals and macromolecular hydroperoxides were build based on standard geometries and fully optimized by means of AM1 and PM3 methods. Then, structural parameters were estimated based on PM3 semi-empirical quantum chemical computations implemented in the software package HyperChem Release 6.01 for Windows [10].

RESULTS AND DISCUSSION

Bond strengths in polypropylene macroradicals and hydroperoxides

The bonds orders and bonds lengths in polypropylene macromolecules and macroradicals as well as macromolecular hydroperoxides have been shown in Scheme 1. The presented data indicate that both secondary and tertiary alkyl macroradicals of polypropylene have weakened bonds in β -position to radical site (dashed lines). The bond weakening is rather small: the bond orders equal 0.97 versus 0.98 in initial PP macromolecule (see Scheme 1a—c). More weakened β -bonds appeared in PP-oxy macroradicals (Scheme 1d, e). In that case the in-chain bond orders from 0.93 to 0.95 indicate increased susceptibility to main chain scission reactions. One more possible reaction is β -scission of a side bond resulting in hydrogen atom or methyl radical breaking



Scheme 1. Bond order (numerator) and bond length (denominator) in polypropylene macromolecule and its degradation intermediates

off (bond order equals to 0.88 and 0.94, respectively). In that case the arising in-chain ketone group is an UV-chromophore which may initiate further photooxidation *via* Norrish Type I reaction [2]. In consequence, PP-oxy macroradicals appear to affect chain scission reactions *via* two different modes.

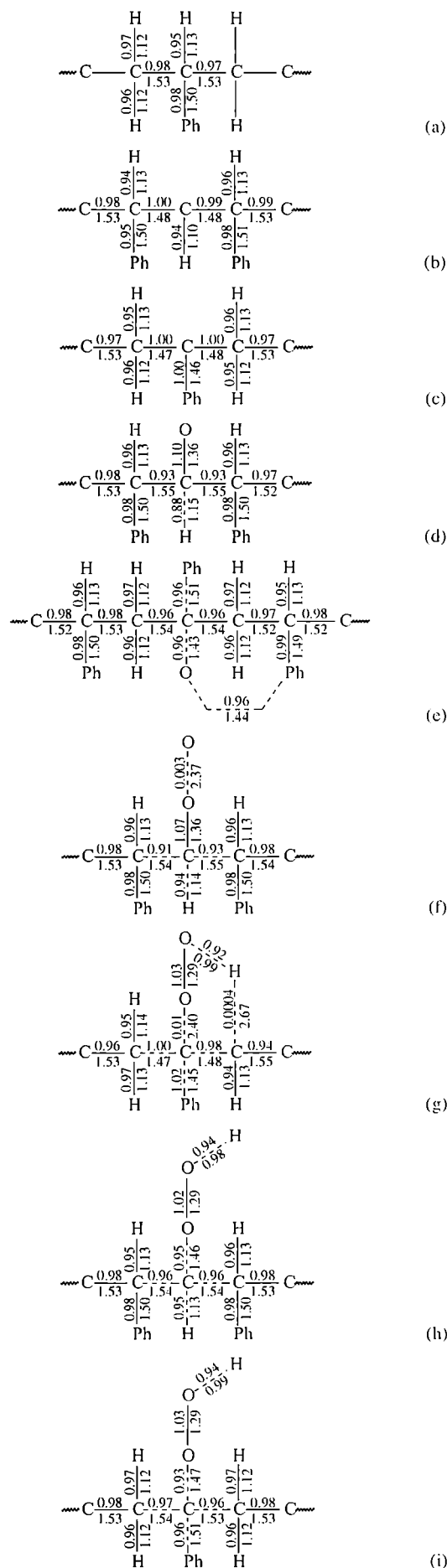
Both tertiary and secondary PP-peroxy macroradicals show the main chain bonds strengths slightly decreased in the nearest neighborhood to the reactive group — the weakened bond orders equal 0.97 (Scheme 1f, g). At the same time, in both the macroradicals the C-O bond looks far less stable (bond orders for secondary and tertiary peroxy macroradical are equal 0.87 and 0.85, respectively). Apparently, both the polypropylene peroxy macroradicals may decompose resulting in oxygen molecule and alkyl macroradical (reverse reaction to that of peroxy macroradical formation). A quite similar picture can be seen in PP-hydroperoxides as well (see Scheme 1h, i). Here the most possible products of decomposition are hydroperoxy radical and alkyl macroradical.

One can conclude that the main pathway of polypropylene backbone chain breakage is β -scission of oxy macroradicals. Main chains in polypropylene alkyl and peroxy macroradicals as well as hydroperoxides look rather stable.

Bonds strengths in polystyrene macroradicals and hydroperoxides

The bonds orders and bonds lengths in polystyrene macromolecules and macroradicals as well as macromolecular hydroperoxides have been shown in Scheme 2. In contrast to polypropylene, weakened β -bonds in the main chain of polystyrene alkyl macroradicals rather do not appear: bonds orders range from 0.97 to 0.99 (Scheme 2b, c) in comparison with 0.97—0.98 for the initial macromolecule (Scheme 2a). This fact may be explained considering the side phenyl groups may act as donors of electron density. At the same time, isomeric PS-oxy macroradicals proved to have quite different structures. In the case of secondary oxy macroradical, β -bonds show markedly decreased order (0.93) indicating increased susceptibility to polymer chain scission. In parallel, hydrogen atom may also split off (bond order equals 0.88) what results in formation of in-chain ketone (Scheme 2d). On the other hand, in the case of tertiary PS-oxy macroradical the bond weakening is very small (Scheme 2e). Probably, this macroradical structure is stabilized by intramolecular interaction between oxygen atom and phenyl group (see ref. [8] for details).

Scheme 2. Bond order (numerator) and bond length (denominator) in polystyrene macromolecule and its degradation intermediates



Polystyrene secondary and tertiary peroxy macroradicals have quite different structures as well. Secondary peroxy macroradical has quite weakened main chain bonds in the neighborhood of peroxy group (bond orders range from 0.91 to 0.93 — see Scheme 2f). In addition, the very weak O-O bond (Scheme 2f) may result in easy transformation into secondary oxy macroradical, which is as well inclined to β -scission (see above). On the other hand, tertiary PS-peroxy macroradical proved an interaction between the terminal peroxide oxygen atom and neighbor hydrogen atom resulting in very weak C-O and C-H bonds (Scheme 2g). In that case, the most probable transformation way is formation of hydroperoxy radical and in-chain double bond. Polystyrene hydroperoxides (both secondary and tertiary ones) have in-chain β -bonds slightly weakened — the bond order is 0.96–0.97.

One can summarize that polystyrene alkyl macroradicals play rather minor role in macromolecule scission. It is believed, that the main active intermediates in that reaction are secondary oxy and peroxy macroradicals.

CONCLUSIONS

The polymer degradation intermediates have been simulated with the aim to indicate weakened bonds as possible sites of main chain scission. The minimal bond strengths have been found in the main chains of both secondary and tertiary polypropylene oxy macroradicals. Apparently, β -scission of alkyl macroradicals does

not play a significant role in polypropylene degradation. Alkyl macroradicals of polystyrene have no weakened bonds in the main chain. Among oxygen containing PS intermediates the *sec*-oxy and *sec*-peroxy macroradicals look as those having increased susceptibility to chain scission according to β -scission mechanism. The reactions of decomposition of peroxides [equation (3)] as well as isomerization of oxy macroradicals [equation (4)] seem less probable to occur.

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