Polymer Bulletin 15, 531–537 (1986)

Polymer Bulletin

Initiated Oxidation of PE and PP in Solution

M. Iring[1], **T. Kelen**[1,2], **and F. Tüdős**[1,3]*

[1] Central Research Institute of Chemistry of the Hungarian Academy of Sciences, P.O.Box 17,
H-1525 Budapest, Hungary
[2] Kossuth Lajos University, Institute of Applied Chemistry, H-4010 Debrecen 10, Hungary
[3] Eötvös Loránd University, Department of Chemical Technology, Múzeum krt. 6–8,
H-1088 Budapest, Hungary

Summary

A study was made on the oxidation of a low density polyethylene and of an isotactic and an atactic polypropylene in solution. The solvent was 1,2,4-trichlorobenzene and the process was investigated at different temperatures, with varying concentrations of the initiator and of the polymer. Under the experimental conditions, a non-accelerating chain reaction proceeds at the beginning of the process. The equation derived from the proposed simplified mechanism describes consistently the dependences of experimentally measured rates on the concentrations of the initiator and of the polymer.

Introduction

Several publications indicate that the oxidation of PE and PP are processes of interest and of importance, but of very high complexity not yet clarified and composed of many elementary steps.

The study of those processes discloses several phenomena which cannot be explained by merely chemical factors. Several experimental observations prove that the mechanism and rate of oxidation of a homopolymer free of additives is highly influenced, among others, by the following factors: molecular mass, orientation of the chains, qualitative and quantitative characteristics of crystallinity, phase state, structural defects and chemical environment of the polymer chain. The majority of these factors slightly affects the mechanism and rate of primary initiation process of the oxidation (these are mainly determined by the chemical structure of the polymer). Recently, we dealt with the connection between the extent of chain orientation and the mechanism of primary initiation [1].

Fig. 1 shows the dependences of the induction period (t_i) and of the maximum rate ($W_{O_2,max}$) of isotactic polypropylene (IPP) autooxidation on the thickness of the layer ($1/g_o$ is the reciprocal mass). Fig.2 illustrates the temperature dependences of the induction period and of the maximum rate of low density polyethylene (PE). The t_i value is independent of the layer thickness (IPP, t_i vs. $1/g_o$ plot) and of the phase state (PE, $\ln(1/t_i)$ vs. $1/T$ plot). However, the layer thickness and the temperature considerably influence the rate and even the mechanism of the further elementary steps of the chain reaction, especially of the chain propagation and termination. This is well illustrated by the W_{max} vs. $1/g_o$ (IPP, Fig.1) and $\ln(W_{max})$ vs. $1/T$ (PE, Fig.2) plots. The maximum rate of oxygen uptake of IPP above the critical thickness rapidly decreases with the further increase of the thickness. The $\ln(W_{max})$ vs. $1/T$ plot shown for PE has a break near the melting point, indicating that the rate of the process depends on the phase state in this stage of the oxidation. If some physical factors are eliminated, for example, by working in solution, then the main features of the process can surprisingly well be described by a simple chemical scheme introduced by

---

* To whom offprint requests should be sent

Bolland and Gee [2].

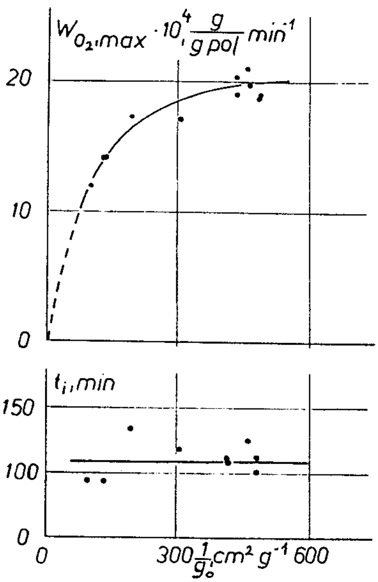


Fig. 1: Dependence of t_i and $W_{O_2,max}$ on layer thickness in IPP oxidation.

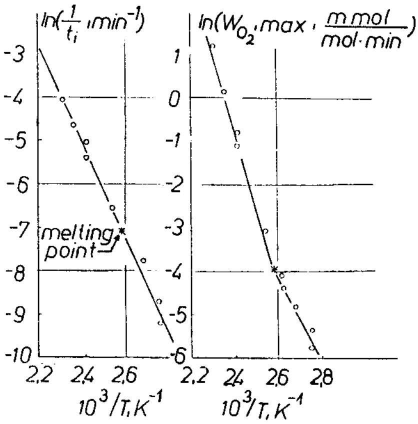


Fig. 2: Temperature dependence of t_i and $W_{O_2,max}$ in PE oxidation.

Further on, we present our experimental results concerning the oxidation of PE, of IPP and of atactic polypropylene (APP) in solution, initiated by dicumyl peroxide (DCP), and the dependence of the oxidation rate on the temperature and on the concentrations of initiator and of polymer, together with kinetical description.

In Table 1, some characteristics of purified, additive-free polymers are summarized.

Table 1.

	PE	IPP	APP
Density, g/cm^3	0.922	0.910	0.851
$\overline{M}_n \cdot 10^{-3}$	26	57	4.5
Polydispersity	6.5	5.4	4.6
Semicrystalline melting point, °C	113	165	-
Melt index	0.3/10 min/190 °C	1.4/10 min/230 °C	-
Isotactic proportion, %	-	>95	5
Average size of crystallites, Å	128	159	-
Crystalline proportion, %	57	61	-
$[-OOH]_0$, mmol/g	$\sim 1.5 \cdot 10^{-3}$	-	$\sim 4 \cdot 10^{-4}$
$[{>}CO]_0$, mmol/g	$\sim 2.0 \cdot 10^{-3}$	-	$\sim 3.6 \cdot 10^{-2}$
Short chain branching	12/1000 C atoms	-	-

Table 2. contains the experimental conditions, relationships investigated and notations.

Table 2.

Experimental conditions	Notation	Unit	Range
Solvent: 1,2,4-trichlorobenzene	TCB		
Temperature	T	^{o}C	90-130
Oxygen pressure	p	kPa	~95
Polymer concentration	[RH]	mol m.u./l*	0.07-2.3
Initiator: (dicumyl peroxide) concentration	[DCP]	mol/l	$0.01 \cdot 10^{-2}$-$8.5 \cdot 10^{-2}$

Relationship investigated: The dependence of the initial rate of oxygen uptake (W_0) of the polymer on the temperature and on the concentrations of the polymer and initiator.

*m.u. = monomeric unit

Results

The time dependence of oxygen uptake in the initiated oxidation of the three polymers and of the initiator alone are illustrated in Fig.3 by the ΔO_2 vs. t plots. All the plots are linear. As can be seen, PE has a threefold lower rate of oxygen uptake compared to both PP samples.

The difference between the rate is caused by the difference of chemical structures of the polymers; the tertiary hydrogen atoms in PP have a lower bond energy than the secondary hydrogen atoms in PE.

The oxidation rates of IPP and APP differ only slightly under the given conditions; interestingly the initial rate of oxygen uptake of IPP is somewhat (by cca 30 %) higher than that of APP, contrarily to the findings for condensed phase [3,4].

The dependences of initial rates of oxygen uptake of polymer solutions on the initiator concentration are shown in Fig.4 in linear and logarithmic scale. The figure contains also the concentration dependence of the rate of DCP oxidation.

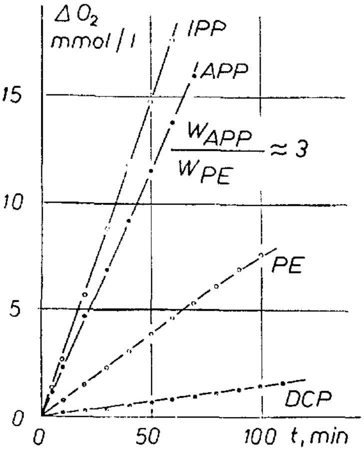


Fig.3: Kinetics of oxygen uptake in the initiated oxidation at 120 ^{o}C ($[DCP]_0 = 1.48 \cdot 10^{-2}$ mol/l, $[RH]_0 = 0.56$ mol m.u./l)

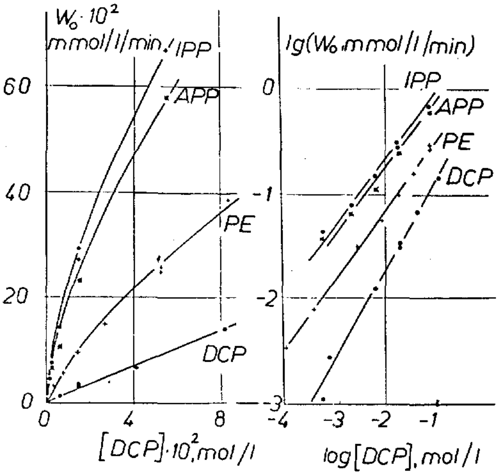


Fig.4: Dependence of W_0 on $[DCP]_0$ concentration at 120 ^{o}C. ($[RH]_0 = 0.56$ mol m.u./l).

For the latter, the virtual reaction order related to the initiator is approximately 1, for the three polymers it is about 0.7.

The temperature dependence of the initial rate of oxygen uptake for the polymers and for DCP is shown in Fig.5. The initial rate of oxygen uptake increases uniformly, with an activation energy of about 126 kJ/mol, for all the four systems studied; the rate of initiation is determined by the rate of thermal decomposition of DCP also for the polymers.

The rate of IPP oxidation is somewhat higher than that of APP oxidation at all temperatures investigated in accord with the observations of Van Sickle [5] for other conditions. The difference may be caused by the combination of the following two factors: the higher probability of intramolecular chain propagation in IPP oxidation (due to stereoregularity) than in APP oxidation, and a higher rate of initiation in APP oxidation, due to the higher concentration of structural defects. In autoxidation these two effects will compensate each other, in an initiated process, however, where the rate of initiation is determined at the beginning solely by the thermal decomposition of DCP, the rate of IPP oxidation is higher.

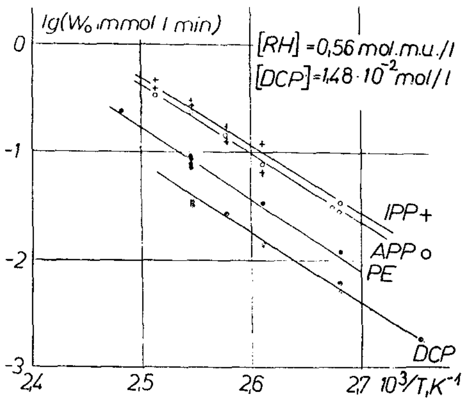


Fig.5: Temperature dependence of W_0 in solution.

The dependence of the rate of oxidation on the polymer concentration is illustrated by Fig.6. The rates belonging to the same [RH] value are considerably higher for the two kinds of PP than for PE. The slopes and intercepts of the straight lines were calculated by Equ. (17) (see further on), using the values $\alpha = 0.8$, $f' kd = 3.28 \cdot 10^{-4}$ min^{-1} and the $k_2/\sqrt{k_4}$ data of Table 3. As can be seen, the deviations of experimental data from the calculated straight lines increase with the concentration of RH.

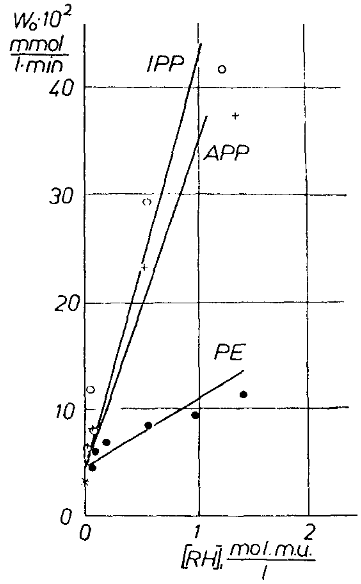
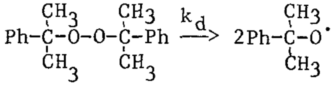


Fig.6: Dependence of W_0 on polymer concentration at 120 °C ($[DCP]_0 = 1.48 \cdot 10^{-2}$ mol/l)

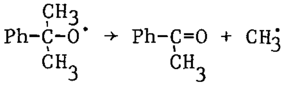
Evaluation

The initiated oxidation of polymers is a complex process in which different elementary reactions of initiator oxidation and those of initiated and autooxidation of the polymer are combined.

The main elementary steps of the oxidation of dicumyl peroxide are:

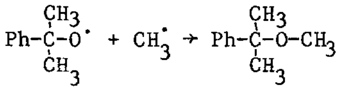


$$\mathrm{Ph{-}C(CH_3)_2{-}O{-}O{-}C(CH_3)_2{-}Ph} \xrightarrow{k_d} \mathrm{2Ph{-}C(CH_3)_2{-}O^{\bullet}} \tag{1}$$



$$\mathrm{Ph{-}C(CH_3)_2{-}O^{\bullet}} \rightarrow \mathrm{Ph{-}C(CH_3){=}O} + \mathrm{CH_3^{\bullet}} \tag{2}$$

$$\mathrm{CH_3^{\bullet}} + \mathrm{O_2} \rightarrow \mathrm{CH_3O_2^{\bullet}} \tag{3}$$



$$\mathrm{Ph{-}\underset{CH_3}{\overset{CH_3}{C}}{-}O^{\bullet}} + \mathrm{CH_3^{\bullet}} \rightarrow \mathrm{Ph{-}\underset{CH_3}{\overset{CH_3}{C}}{-}O{-}CH_3} \qquad (4)$$

The thermal decomposition of initiator (I) is the rate determining process, thus in terms of Reactions (1) to (4), the following "stoichiometric" equation can be given:

$$I(+2f'O_2) \xrightarrow{k_d} 2f'R'O_2^{\bullet} + \text{product} \qquad (5)$$

where f is the radical efficiency factor and R' denotes the methyl group.

If the system contains only dicumyl peroxide, no further oxygen consumption should be assumed in the inert solvent and the peroxy radicals undergo bimolecular termination. The quantity of the oxygen liberated in the termination reaction is neglected in this simplified treatment.

Thus, the rate of oxygen absorption in the system containing only initiator is described by the following relationship:

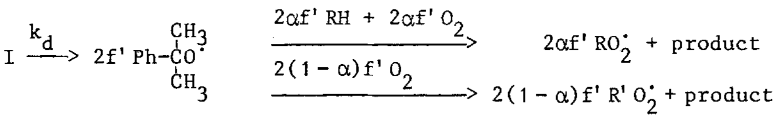
$$W = 2f'k_dI = 2f'k_dI_0e^{-k_dt} \qquad (6)$$

where I_0 stands for the initial concentration of DCP. The experimental Arrhenius plot based on the initial rate of DCP oxidation is the following:

$$f'k_d = 2.57 \cdot 10^{13} \exp(-125.5\ [\mathrm{kJ/mol}]/RT) \quad \mathrm{min}^{-1} \qquad (7)$$

From this, the value of $f'k_d$ belonging to 110 °C was calculated and $8.4 \cdot 10^{-6}$ sec^{-1} was found. Considering that for the rate constant of the thermal decomposition of DCP, $8 \cdot 10^{-6}$ sec^{-1} to $11 \cdot 10^{-6}$ sec^{-1} had been determined at 110 °C in different solvents [6], the approximative value of f' is 0.8 to 1.0 which seems acceptable. Also the experimentally determined activation energy is in a rather good agreement with the literature data (~144 kJ/mol) [6]. This suggests that the rate determining step of DCP oxidation is the thermal decomposition of the initiator. The same is indicated by the experimental value of about 1 of the virtual reaction order of oxygen absorption related to DCP.

The initiated oxidations of PE, IPP and APP are initiated partly by the methyl peroxide radicals ($R'O_2^{\bullet}$) originated from the DCP decomposition, however, in the presence of the polymer, also the initiating effect of the cumyl peroxy radicals on the oxidation must be considerable. The main processes of the initiation of polymer oxidation (of the formation of macroradicals) can be approximated by the following scheme:



$$I \xrightarrow{k_d} 2f'\,\mathrm{Ph{-}\underset{CH_3}{\overset{CH_3}{C}}O^{\bullet}} \begin{array}{l} \xrightarrow{2\alpha f'RH + 2\alpha f'O_2} 2\alpha f'RO_2^{\bullet} + \text{product} \\ \xrightarrow{2(1-\alpha)f'O_2} 2(1-\alpha)f'R'O_2^{\bullet} + \text{product} \end{array} \qquad (8)$$

where α denotes the probability of initiation by cumyl peroxy radicals.

The scheme of initiation by methyl peroxy radicals taking place with the probability of $1-\alpha$ is:

$$R'O_2^{\bullet} + RH(+O_2) \rightarrow R'O_2H + RO_2^{\bullet} + \text{product} \qquad (9)$$

Combination of Equs.(8) and (9) yields the whole initiation:

$$I[+2f'RH + 2(2-\alpha)f'O_2] \xrightarrow{k_d} 2f'RO_2^{\bullet} + \text{product} \qquad (10)$$

The chain propagation processes for the initiated oxidation are

$$RO_2^{\bullet} + RH \xrightarrow{k_2} RO_2H + R^{\bullet} \qquad (11)$$

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \qquad (12)$$

With sufficiently high oxygen pressure, Process (12) goes very fast; in this case, by combining Equs.(11) and (12), we obtain

$$RO_2^{\bullet} + RH(+O_2) \xrightarrow{k_2} RO_2^{\bullet} + RO_2H \qquad (13)$$

The termination is the bimolecular reaction of $RO_2^{\bullet}$ radicals

$$RO_2^{\bullet} + RO_2^{\bullet} \xrightarrow{k_4} \text{product} \qquad (14)$$

In the treatment of the reaction, we assume that, under the conditions of initiated oxidation, the decomposition of polymer hydroperoxide formed in Process (11) is negligibly slow. The oxygen formed in Process (14) is not considered either. The cross termination which can take place with the initiator radicals is also neglected.

The steady radical concentration according to Equ.(16) can be calculated from Equ.(15), and the rate of the oxygen absorption (W) is given by Equ.(17).

$$\frac{d[RO_2^{\bullet}]}{dt} = 2f'k_dI - 2k_4[RO_2^{\bullet}]^2 = 0 \qquad (15)$$

$$RO_2^{\bullet} = \sqrt{f'k_dI/k_4} \qquad (16)$$

$$W = 2(2-\alpha)f'k_dI + k_2/\sqrt{k_4}\cdot\sqrt{f'k_dI}\cdot[RH] \qquad (17)$$

The dependences of the initiated oxidation on the concentrations of the initiator and of the hydrocarbon can be investigated with the use of Equ.(17), dividing it by the initial concentration of the initiator (I_0), we obtain

$$W_0/I_0 = 2(2-\alpha)f'k_d + k_2/\sqrt{k_4}\cdot\sqrt{f'k_d}\cdot[RH]_0/\sqrt{I_0} \qquad (18)$$

The experimental data are plotted by Equ.(18) in Fig.7.

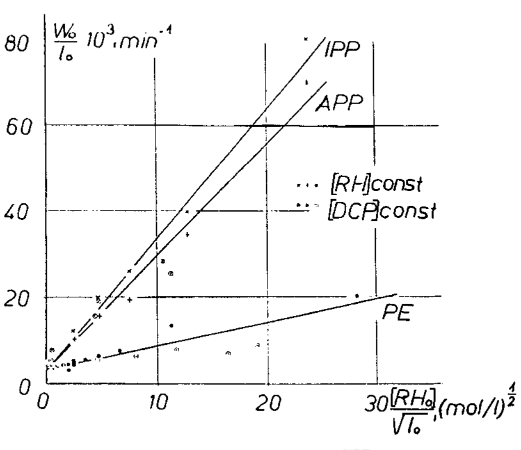


Fig.7: The W_0/I_0 vs. $[RH]_0/\sqrt{I_0}$ plots in the initiated oxidation in solution at 120 °C.

Linearization gives rather straight lines for all the three polymers. As it has been assumed, the intercepts are in rather good agreement for the three polymers. This verifies that the rate of initiation is determined by the thermal decomposition of DCP, and secondary initiation processes cannot prevail at the beginning of the process.

Using Equ.(7), the value of α is determined from the intercept, uniformly 0.8 was obtained, which means that only 20 per cent of the cumyloxy radicals undergo transformation in the presence of hydrocarbons. The $k_2/\sqrt{k_4}$ rate constants for 120 °C, calculated from the slopes are listed in Table 3.

Table 3.

Polymer	$k_2/\sqrt{k_4}\cdot10^{-3}$ $(l\cdot mol^{-1}min^{-1})^{1/2}$	
PE	14.4	
IPP	88.5	$\alpha\sim0.8$
APP	69.9	

The $k_2/\sqrt{k_4}$ values obtained from the data measured at different temperatures using Equ.(17) are presented in Fig.8 and in Table 4 ([RH] = 0.56 mol m.u./l, $[DCP]_0 = 1.48\cdot10^{-2}$ mol/l). In the table, also the calculated Arrhenius parameters are listed.

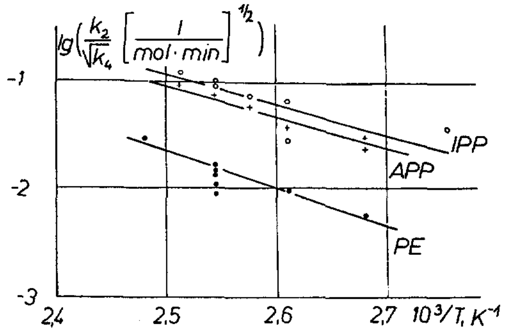


Fig.8: Temperature dependence of $k_2/\sqrt{k_4}$ in initiated oxidation in solution.

Table 4.

T, °C	$k_2/\sqrt{k_4} \cdot 10^3$ $(l \cdot mol^{-1} min^{-1})^{1/2}$		
	PE	IPP	APP
90	-	37.01	-
100	5.76	-	27.04
110	9.87	47.48	38.24
115	-	60.06	57.37
120	13.42	94.89	73.54
125	-	109.30	92.35
130	30.31	-	-
A, $(l \cdot mol^{-1} min^{-1})^{1/2}$	$2.12 \cdot 10^6$	$2.97 \cdot 10^6$	$2.26 \cdot 10^6$
E, kJ/mol	61.2	56.5	56.5

References

1. N.Ya.Rapoport, L.S.Shibryaeva, V.E.Zaikov, M.Iring, Zs.Fodor, F.Tüdős, Polym.Degrad.Stab. 12, 191 (1985)
2. J.L.Bolland, Proc.R.Soc. 186, 230 (1946), J.L.Bolland and G.Gee, Trans. Faraday Soc. 42, 236 (1946)
3. F.R.Mayo, Macromolecules 11, 5 942 (1978)
4. M.Iring, Zs.László-Hedvig, F.Tüdős, T.Kelen, Polym.Degrad.Stab. 5, 467 (1983)
5. D.E.Van Sickle, J.Polym.Sci. Part A-1 10, 355 (1972)
6. V.L.Antonowskii, "Organicheskie Perekisnye Initsiatory", Izd. Khimia, Moskva (1972)

Accepted June 9, 1986