Mechanism and Kinetics of Polyethylene Crosslinking by α,α'-Bis(*tert*-butylperoxy)-*p*-diisopropylbenzene*

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Synopsis

The study of the mechanism of polyethylene crosslinking is realized by a kinetic analysis of the α,α-bis(*tert*-butylperoxy)-*p*-diisopropylbenzene decomposition, as well as by the determination of its decomposition products and crosslink formation in the polymer. The experiments were carried out in a temperature range of 118°–148°C in both polyethylene and its low-molecular model, *n*-octane. From the results obtained it follows that the peroxide decomposition in both hydrocarbon media is kinetically a unimolecular reaction with an activation energy of 36 ± 2 kcal/mole and with an equivalent participation of both peroxidic groups, whereby a biradical formation is improbable. Macroradicals arise by a dehydrogenization reaction in which mainly primary oxyradicals of various types take part and methyl radicals are also formed by a transformation process of the former. Both types of radicals decay exclusively in a substitution reaction with polymer chains. The whole process is terminated by macroradical recombination so leading to crosslink formation in polyethylene.

INTRODUCTION

In polyethylene (PE) crosslinking only peroxides with higher decomposition temperature are used for technologic reasons. One of these particularly suitable initiators of the PE crosslinking reaction is, in addition to dicumyl peroxide, α,α'-bis(*tert*-butylperoxy)-*p*-diisopropylbenzene (14P):
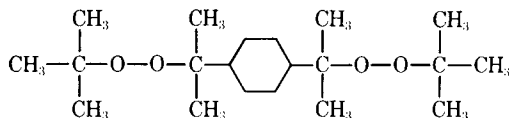
As this source of free radicals contains two peroxidic groups in one molecule and the decomposition reaction of such a case has not yet been investigated, we analyzed the sequence of the elementary processes leading to crosslink formation in PE by a homolytic cleavage of such a peroxide. We investigated the mechanism and kinetics of this peroxide decomposition simultaneously in a low-molecular model medium, *n*-octane.

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EXPERIMENTAL

The PE used in this work was a commercial low-density native product (Slovnaft, Bratislava) with a specific gravity of 0.921 g/cm³ and melt index 2.1 g/10 min. Its trademark is Bralen KB-2-11.

The chosen low-molecular hydrocarbon model, n-octane, was rectificated and the fraction boiling from 125.5° to 125.8°C was used.

The peroxide (14P) was purified by recrystallization from its ethanolic solution and the content of active oxygen in the purified product was found to be 9%.

The peroxide was added to the PE melt at 117°C (under a nitrogene atmosphere) by 5 min mixing in the mixer of a Brabender plastograph. These samples were then heated in sealed glass tubes filled with purified nitrogen using an air-circulating oven. These samples were predominantly immersed in an oil bath to reach quickly the reaction temperature. The preheating time in comparison with the time of reaction was negligible.

After this procedure, the undecomposed peroxide was isolated from the polymer by 48 hr of extraction with benzene in a Soxhlet apparatus, where the solvent was regularly changed after 8-hr periods. The PE sol fraction precipitated in the cooled extract was removed by filtration and, evaporating the solvent from the filtrate, the peroxide was isolated. The amount of peroxide was determined iodometrically after its reduction with natrium-jodid in boiling glacial acetic acid and water.[2] As this method applied to 14P gave only 95% results of theoretical, the obtained results were corrected from this point of view. The 14P decomposition products (acetone and *tert*-butanol) were isolated from 50 mg PE samples by 24 hr of extraction at room temperature with n-heptane and analyzed by GLC method. The chromatographic column was filled with Chromosorb W impregnated with 15% of silicone elastomer SE-30. The working temperature was 80°C.

TABLE I
Peroxide decomposition in PE at 129.5°C and
in n-octane at its boiling point, after 330 minutes[a]

Polyethylene		n-Octane	
$[14P]_0$, mole/kg	$\log \dfrac{[14P]_0}{[14P]_t}$	$[14P]_0$, mole/kg	$\log \dfrac{[14P]_0}{[14P]_t}$
0.0437	0.409	0.0180	0.268
0.0580	0.345	0.0355	0.268
0.0722	0.391	0.0589	0.271
0.0802	0.382	0.0765	0.262
0.1000	0.392	0.0996	0.264
0.1138	0.404	0.1185	0.273
0.1274	0.358	0.1474	0.266
		0.1773	0.261
		0.2069	0.269

[a] $[14P]_0$ is initial peroxide concentration and $[14P]_t$, its concentration after the decomposition reaction.

The PE crosslinking was measured from its sol fraction, determined by extraction with boiling CCl_4,[3] and the results were corrected with regard to the amount of added peroxide.

The contents of undecomposed peroxide as well as its decomposition products (acetone, tert-butanol) in n-octane were determined by the same analytic methods as in PE. With regard to the nature of this reaction medium, all experimental procedures were simpler, of course. The heating of the samples was in this case carried out in a thermostated silicone oil bath, except for the results presented in Table I, which were obtained at a temperature maintained by the boiling of n-octane under purified nitrogen.

The α,α'-bis[hydroxy(p-diisopropylbenzene)diol] formed by the decomposition of 14P in n-octane was determined by GLC method, using a column filled with Chromosorb W and 3% of neopentyl glycol succinate, with a programmed temperature increase from 120° to 180°C at a rate of 12.5°C/min. α-Naphtol was used as inner standard.

RESULTS

The results of peroxide decomposition in PE as well as in n-octane obtained in the above described manner in dependence on the initial 14P concentration at constant temperature are given in Table I.

The decomposition of 14P in PE and n-octane at various temperatures was determined analogously and is shown in Table II.

The rate constants of unimolecular peroxide decomposition calculated from these results according to the Arrhenius equation are illustrated in Figure 1.

The content of acetone and tert-butanol formed by peroxide decomposition in PE and the simultaneously caused decrease of the polymer solubility in dependence of the initial 14P concentration is given in Table III. The time dependence of acetone, tert-butanol and diol formation by 14P decomposition in n-octane is summarized in Table IV.

TABLE II
Decomposition of 14P in PE[a] and n-Octane[b] at Various Temperatures

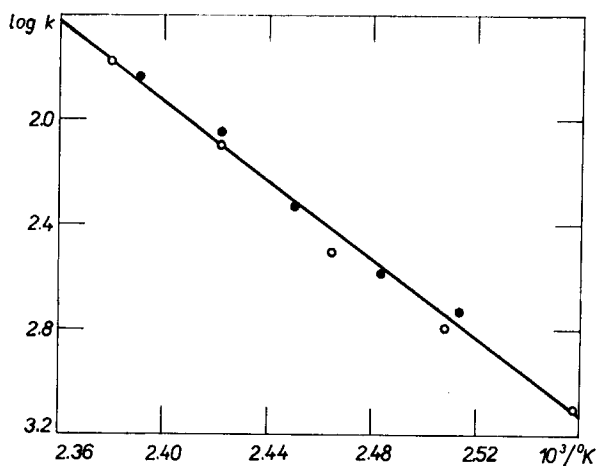| Medium	Temperature, °C	Time, min	$[14P]_t$, mole/kg
PE	125	420	0.0387
	130	300	0.0388
	135	210	0.0318
	140	90	0.0377
	145	60	0.0349
n-Octane	118	495	0.0680
	125.6	360	0.0574
	133	270	0.0445
	140	150	0.0313
	147.2	60	0.0371

[a] $[14P]_0 = 0.0843$ mole/kg.
[b] $[14P]_0 = 0.0986$ mole/kg.

Fig. 1. Logarithmic values of rate constants of unimolecular decomposition (k) of 14P versus reciprocal values of absolute temperature: ($\bullet$) PE; ($\bigcirc$)n-octane.

TABLE III

Polymer Crosslinking Expressed by its Sol Fraction s and Formation of 14P Decomposition Products in PE After 60 Hr at 129.5°C

[14P]$_0$, mole/kg	s	Acetone, mole/kg	tert-Butanol, mole/kg
0.0056	—	0.0011	0.0101
0.0084	—	0.0013	0.0152
0.0143	—	0.0019	0.0250
0.0199	0.265	0.0030	0.0356
0.0278	0.180	0.0043	0.0482
0.0360	0.136	0.0079	0.0630
0.0442	0.107	0.0068	0.0788
0.0551	0.083	—	—
0.0681	0.062	0.0082	0.1216

TABLE IV

Decomposition Products of 14P in n-Octane at 125.6°C[a]

Time, min	Acetone, mole/kg	tert-Butanol, mole/kg	Diol, mole/kg
60	0.0014	0.0098	—
90	0.0021	0.0146	0.0040
120	0.0023	0.0183	0.0054
180	0.0036	0.0270	0.0084
240	0.0049	0.0361	0.0111
360	0.0058	0.0469	0.0157
540	0.0076	0.0612	0.0208
840	0.0089	0.0752	0.0266
4320	0.0115	0.1006	0.0349

[a] Initial peroxide concentration 0.0559 mole/kg.

The results given in Tables I to IV represent average values of at least three parallel measurements.

DISCUSSION

The analysis of the results obtained leads to the identification of the following elementary processes of the PE crosslinking reaction by this peroxide:

Reaction of Radical Formation

The radical process of the crosslinking is initiated by peroxide decomposition which, as can be seen from the constant ratio of log $[14P]_0/[14P]_t$ practically independent of $[14P]_0$ (Table I), follows exclusively a unimolecular mechanism. This fact agrees with the general concept according to which the tertiary peroxides show no tendency to induced decomposition.[4]

The temperature dependence of this reaction rate constant, according to the results from Figure 1 for both PE and n-octane, is expressed practically by an Arrhenius equation

$$k = 1.7 \times 10^{17} \exp\left\{\frac{-36 \pm 2 \text{ kcal}}{RT}\right\} \text{ min}^{-1} \tag{1}$$

from which it follows that in the investigated temperature range there is no remarkable difference between the kinetics of the decomposition of this peroxide in high molecular and low molecular hydrocarbon media.

The value of the activation energy of 14P decomposition is in the range of that for dicumyl peroxide (32–35 kcal/mole)[5] and for tert-butylperoxide
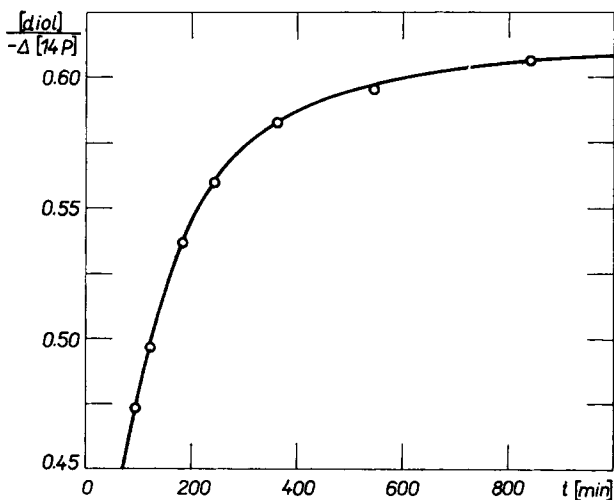

Fig. 2. α,α'-Bis(hydroxy)-p-diisopropyl benzene (diol) formation expressed by its ratio to the decomposed peroxide in n-octane versus reaction time at a temperature of 125.6°C and at $[14P]_0 = 0.559$ mole kg.

(37–39 kcal/mole)[6] in solvents. From this aspect the intermediate position of 14P is connected with its structure where the peroxidic bond is stabilized with cumyl as well as with *tert*-butyl groups.

From this point of view of decomposition, both peroxidic groups are kinetically equivalent not only in the original molecule but also practically after dissociation of one of them. This conclusion is based on the results of the determined ratio of diol/decomposed peroxide in *n*-octane (Fig. 2). Namely, its growth during the decomposition reaction indicates that the rate of cleavage of the second —O—O— group after the primary dissociation of the original peroxidic molecule increases with the accumulation of the product of this primary dissociation, which still carries further peroxidic bond. As the stabilization of the discussed ratio at the investigated temperature begins after ca. 400 min, i.e., approximately after one half-life period of the peroxide decomposition (from the results in Fig. 1, 430 min under these conditions), it can be concluded that the values of the rate constants of cleavage of both peroxidic groups are very close, meaning that the formation of biradicals is wholly improbable.

Transformation Reactions of Primary Radicals

From the above it follows that the complete decomposition of a 14P molecule gives successively four free radicals undergoing a transformation reaction before their decay by a substitution reaction with the medium, as is already known from the decomposition of both *tert*-butyl and dicumyl peroxide, the primary radicals of which may further dissociate to form methyl radicals and the corresponding ketone.[7]

From the results in Tables III and IV it follows that the *tert*-butyl radicals formed by dissociation of both peroxidic groups are partly decomposed on leaving acetone, so that the fraction of decomposed radicals, which can be calculated from the determined ratio of acetone and *tert*-butanol, is in the case of PE 0.09 ± 0.01 and in the case of *n*-octane 0.13 ± 0.01.

The oxy radicals from the middle part of the 14P molecule are also decomposed by a similar mechanism forming methyl radicals and the corresponding ketone, as follows from the fact that the diol content determined in the region of its limit ratio to $-\Delta[14P]$ is only 62 mole-% from the theoretical amount of the decomposed peroxide. In general, the greater inclination to decomposition of such oxy radicals in comparison with *tert*-butoxy radicals is connected with a higher value of the activation energy of methyl radical fission from *tert*-butoxy radicals (13 kcal/mole) rather than cumyloxy radicals (7.3 kcal/mole).[7]

The resulting 14P decomposition products consist of products of radical dehydrogenation of the hydrocarbon (methane, *tert*-butanol, α,α'-bis(hydroxy)*p*-diisopropylbenzene, and 1-acetyl-4-dimethylcarbinolbenzene) as well as of ketones formed by the fission of methyl radicals/acetone and *p*-diacetylbenzene.

Macroradical Formation

As the identified products of 14P decomposition show (Tables III and IV), the macroradicals are formed by a substitution reaction of radicals from the peroxide with hydrogen atoms of the hydrocarbon chain. But a glance at the results in Tables III and IV does not allow to judge the quantitative aspect of this reaction nor the fact whether radicals from the peroxide do not also decay by another mechanism, i.e., whether by addition processes or by radical deactivation interactions.

To clarify this fact we examined the crosslinking efficiency of the peroxide from the values of the change of PE solubility during its crosslinking (Table III). On crosslinking PE with dicumyl peroxide it was found that the concentration of the interpolymer links ($\Delta[n]$) is in a quantitative correspondence with the amount of the decomposed peroxide.[8] For calculating $\Delta[n]$ from the sol fraction, it is possible to apply, for PE of equal types, an equation derived at another occasion[9]:

$$\Delta[n] = -(a + \log s)/b \qquad (2)$$

where a and b have values of 0.522 and 4.88 kg/mole, respectively, in the region of the sol fraction 0.06–0.14 and values of 0.216 and 9.39 kg/mole, respectively, for s in the range 0.14–0.40.

The ratio of the formed crosslinks and the twofold amount of applied 14P calculated according to this procedure has a value of 1.01 $\pm$ 0.03 and in the investigated region does not depend on the peroxide concentration.

From this it follows that radicals from peroxide decay exclusively by a substitution reaction with the hydrocarbon medium and that the other reactions are not of great significance.

Formation of Crosslinks

From the unit efficiency of PE crosslinking by this peroxide, it follows that the interpolymer links are formed exclusively by macroradical combination, which according to this is also the only reaction terminating the radical process of PE crosslinking.

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