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Abstract

Full Text

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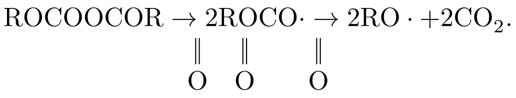
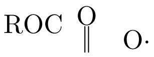
ON THE NATURE OF RADICALS IN THE INITIATION OF POLYMERIZATION BY ORGANIC PEROXYDICARBONATES

In the thermal decomposition of organic peroxydicarbonates, oxy- and carboxyl radicals are formed, initiating polymerization and telomerization reactions (1,2)



$$\mathrm{RO\underset{\underset{O}{\|}}{C}OO\underset{\underset{O}{\|}}{C}OR \rightarrow 2RO\underset{\underset{O}{\|}}{C}O\cdot \rightarrow 2RO\cdot + 2CO_2.}$$

In work (3) it was shown that, when ethylene polymerization is initiated by diethyl peroxydicarbonate, ester end groups are found in the polymer, representing fragments of the initiator incorporated into the polymer. In the present work the radicals participating in the initiation of polymerization of vinyl monomers when dialkyl peroxydicarbonates are used as initiators were studied. The extent of participation of the radicals RO· and



$$\mathrm{RO\overset{\overset{O}{\|}}{C}O\cdot}$$

in polymerization reactions can be estimated by comparing the amount of carbon dioxide liberated during decomposition of the peroxide in the presence and in the absence of monomers, and from the nature of the end groups of polymers obtained in the presence of a percarbonate labeled in the ring with the isotope C^{14}.

Table 1

Decomposition of dicyclohexyl peroxydicarbonate in benzene at 50° in the presence of monomer additives. Duration of the experiment: 18 hours

No.	Monomer	Amount of monomer, mol/l	Initiator taken, g	Initiator taken, g-mol/l	Initiator decomposed, g	Initiator decomposed, g-mol/l	CO_2 evolved, g	CO_2 evolved, mol per 1 mole of decomposed peroxide
1	–	–	6.0045	0.210	5.866	0.205	1.7346	1.92
2	–	–	6.0285	0.211	5.919	0.206	1.7930	1.96
3	Styrene	2.4	2.0064	0.259	1.861	0.240	0.0177	0.063
4	»	2.4	6.1564	0.269	5.891	0.257	0.0469	0.052
5	Methyl methacrylate	2.5	5.9994	0.262	5.732	0.241	0.702	0.8
6	»	2.5	6.0912	0.266	5.539	0.242	0.647	0.76

Table 1 gives data on the amount of carbon dioxide liberated during decomposition of cyclohexyl peroxydicarbonate in benzene in the presence of methyl methacrylate and styrene additives. The data in the table show that the addition of monomers to the reaction system sharply decreases the amount of carbon dioxide evolved. At the same time, the extent of capture by monomers of primary undecarboxylated radicals is not the same. The most

the reaction of the radicals

$$\mathrm{ROC(=O)O\cdot}$$

with styrene proceeds vigorously.

In the presence of methyl methacrylate the rate of reaction of the radicals

$$\mathrm{ROC(=O)O\cdot}$$

with the double bond of the monomer is lower, and a considerable portion of them has time to decarboxylate.

The presence in the polymer of ester end groups was established from the IR spectrum of polystyrene obtained upon initiation of polymerization

Table 2

Activity of polymers obtained with a radioactive initiator

No.	Polymerization temperature, °C	Monomer	Monomer weight, g	Dicyclohexyl percarbonate, g: introduced	Dicyclohexyl percarbonate, g: remaining	Dicyclohexyl percarbonate, g: decomposed	Polymer weight, g	Polymer activity*, imp/min before washing (A_1)	Polymer activity*, imp/min: after washing (A_2)	$\frac{A_2}{A_1}$, %
1	50	Methyl methacrylate	4.0	0.4116	0.257	0.155	1.5758	5030	211	4.2
2	50	»	4.0	0.4420	0.232	0.215	2.5904	9700	401	4.1
3	70	»	4.0	0.3880	0.204	0.184	1.865	930	57	6.1
4	70	»	4.0	0.3950	0.215	0.180	2.035	1046	72	6.9
5	50	Styrene	2.0	0.1951	0.1535	0.0416	0.4150	1546	23	1.5
6	50	»	2.0	0.1937	0.1464	0.0473	0.3640	1750	23	1.3

* Radiometric analysis was carried out on an internal-fill counter. Measurement error $±$3%.

by dicyclohexyl peroxydicarbonate. In the IR spectrum of polystyrene an absorption band in the region of 1720 cm^{-1} is clearly visible, disappearing after treatment of the polymer solution with alcoholic alkali.

In order to confirm the results obtained and to determine the ratio between the amounts of the radicals RO· entering the polymer and

$$ROC(=O)O\cdot$$

polymerization of methyl methacrylate and styrene was carried out in the presence of dicyclohexyl peroxydicarbonate labeled in the ring with radioactive carbon C^{14}.

The starting material for the synthesis of the labeled percarbonate was radioactive phenol. The phenol was hydrogenated to cyclohexanol, from which the percarbonate was then obtained by the method of (4).

Since the amount of initiator fragments entering the polymer is very small, an initiator of high activity (140,000 imp/min) was used, as well as considerable initiator concentrations during polymerization (0.33 g-mol/l). Polymerization was carried out in bulk, in the absence of oxygen, to 15–20% conversion.

A C^{14} balance was not drawn up, since the very high activity of the starting peroxide required large dilutions in determining the activity of the substance, which led to considerable errors in the calculation. For the purpose set in the work, drawing up a balance was not required.

The polymer samples obtained were treated with a solution of potassium iodide in acetic acid to decompose initiator residues and were reprecipitated three times, which ensured complete purification of the polymer from radioactive impurities (5). The prepared samples were subjected to radiometric analysis before and after washing. For washing, a weighed portion of polymer was dis-

were dissolved in acetone and treated with a solution of alcoholic alkali under conditions in which the ester end groups were quantitatively saponified, while groups bound to the polymer chain by a simple ether linkage were not cleaved[6] (see Table 2). It is evident from the table that the content of end groups in polystyrene and polymethyl methacrylate confirms the data given above, namely that the degree of decarboxylation of the radicals

$$\mathrm{ROC}\left(\begin{matrix}\| \mathrm{O} \\ \backslash \mathrm{O}\cdot\end{matrix}\right)$$

in the presence of styrene is lower than in the presence of methyl methacrylate. From these same data it is evident that, with increasing temperature, the number of radicals

$$\mathrm{ROC}\left(\begin{matrix}\| \mathrm{O} \\ \backslash \mathrm{O}\cdot\end{matrix}\right)$$

that undergo decomposition increases, and, accordingly, the degree of participation of RO· radicals in polymerization-initiation reactions increases somewhat.

Thus, in the polymerization of vinyl monomers in the presence of peroxydicarbonates, the radicals formed,

$$\mathrm{ROC}\left(\begin{matrix}\| \mathrm{O} \\ \backslash \mathrm{O}\cdot\end{matrix}\right)$$

interact with the double bond of the monomer at a rate considerably exceeding the rate of their decarboxylation; as a result, the fraction of RO· radicals participating in initiation reactions is insignificant.

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Note: Figure translations are in progress. See original paper for figures.

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