

Decomposition of peroxides of isotactic powdered polypropylene by hydroiodic acid

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Received 12 January 1976

By the method of experimental designing, its statistical evaluation and by using hydroiodic acid we looked for conditions of quantitative decomposition of peroxides of isotactic powdered polypropylene initiating styrene polymerization in the emulsion system in the presence of FeSO_4 —triethylenetetramine chelate.

The degree of decomposition of peroxides of isotactic powdered polypropylene was determined by the results of styrene polymerization in their presence.

The investigated peroxides decompose quantitatively by employing HI in the concentration range 5.5 — 7.58 mol l^{-1} at 70 — 90°C during 6 — 7 h .

These conditions exclude the possibility of simultaneous quantitative determination of peroxides for their thermal decomposition proceeding parallelly at the above-mentioned temperatures.

Методом планированного опыта и его статистической оценкой определены с помощью иодистоводородной кислоты условия количественного распада перекисей изотактического порошкообразного полипропилена, которые инициируют полимеризацию стирола в эмульсионной системе в присутствии внутрикомплексного соединения FeSO_4 —триэтилентетрамина.

Для оценки степени распада перекисей изотактического порошкообразного полипропилена служили результаты полимеризации в его присутствии в полимеризационной системе.

Количественный распад этих перекисей настает при применении HI в концентрационном интервале $5,5$ — $7,58 \text{ моль л}^{-1}$ при температуре 70 — 90°C в течении 6 — 7 часов .

Определенные условия распада этих перекисей исключают возможность их одновременного количественного определения этим способом из-за параллельно проходящего их термического распада при этих температурах.

In the presence of oxidized isotactic polypropylene (PP) and FeSO_4 —triethylenetetramine chelate, a part of styrene is bonded on PP and part of it forms a homopolymer in the emulsion polymerization system [1]. Homo-

polymerization is initiated by products of the decomposition of PP hydroperoxide, whereas binding of a monomer is initiated by radicals formed by decomposition of the more stable PP peroxide, probably of the dialkyl peroxide type. The thermal stability of the peroxides considered is relatively low: hydroperoxide undergoes thermal decomposition already at temperatures above 30°C, more stable peroxide above 40°C [2].

Hydroperoxide of PP exerts negative effect upon formation of the bonded polymer. If it is removed from PP, the rate of modification of PP substantially increases and formation of homopolymer decreases to minimum. On this basis the authors [3] evaluated quantitateness and selectivity of hydroperoxide determination in isotactic powdered polypropylene by iodometric method [3].

The values for conversions of the bonded styrene reflect sensitively the concentration change of both types of peroxides in PP. The loss of hydroperoxide will manifest itself by an increasing conversion of the bonded monomer, the loss of more stable peroxide by a decreasing one.

The aim of the present paper was to look for conditions of the decomposition of more stable peroxide of PP. The degree of decomposition was tested by polymerization; the measure of quantitative decomposition of PP peroxides was the minimum amount of styrene bonded on PP with previously decomposed peroxides. Iodometry was the proper method for peroxide decomposition but a more active decomposition agent was used, *viz.* hydroiodic acid, usually employed for determining the stable substances of the dialkyl peroxide type [4—7].

Experimental

Chemicals

The chemicals used, namely isotactic powdered polypropylene, styrene (ST), triethylenetetramine, FeSO₄, emulsifier Mersol H, water, nitrogen, solvents (chloroform, *n*-heptane, benzene, isopropyl alcohol), glacial acetic acid, KI, Na₂S₂O₃, and starch have been described earlier [3].

Acetic anhydride was of anal. grade.

Hydroiodic acid, unstabilized, pure, was distilled twice before use at normal pressure in a nitrogen atmosphere, azeotrope distilling at 127°C being collected. The HI concentration was 57% (*i.e.* 7.58 mol l⁻¹). By shaking with mercury, the residues of iodine were removed from HI before use.

Anal. grade mercury was employed.

Procedures

Polypropylene was oxidized by means of a fluidization method for 40 min at room temperature by ozone-containing oxygen with concentration 12 mg l⁻¹.

The procedure used for determination or decomposition of PP peroxides: oxidized PP (0.45 g) was evacuated in ampules and nitrogen introduced. HI and other liquid components of the system bubbled through nitrogen (30 min) were added to PP in a nitrogen atmosphere. The ampules were placed after sealing in a revolving frame in a thermostated bath. The isolated iodine was titrated with $\text{Na}_2\text{S}_2\text{O}_3$ using starch as indicator and corrected for unoxidized PP. The peroxides content was given in moles of active oxygen per 1 kg of PP (mol kg^{-1}). If PP was employed in the polymerization system after peroxides determination, it was rid of residues of iodometric decomposition system by washing with a mixture acetone—water and with acetone and vacuum dried at room temperature.

The polymerization has been described earlier [1]. The polymerization system consisted of a solid phase containing PP oxidized for 40 min (0.4 g), of a liquid phase (total volume 15 ml) containing FeSO_4 ($1.33 \times 10^{-3} \text{ mol l}^{-1}$ aqueous phase), triethylenetetramine ($2.00 \times 10^{-3} \text{ mol l}^{-1}$ aqueous phase), emulsifier ($9.75 \times 10^{-3} \text{ mol l}^{-1}$ aqueous phase), and of an organic phase represented by styrene (3 ml). After 3 h polymerization at 35°C the modified PP was separated from the emulsion by filtration and unbonded homopolystyrene was precipitated with methanol. In both cases conversion was expressed in % of reacted styrene with regard to the initial amount (% of bonded ST and homopolymer, respectively).

Results and discussion

When attempting to act by hydroiodic acid on peroxides of isotactic powdered PP, it was necessary to contact them since HI even at its maximum concentration of distilling azeotrope does not wet sufficiently PP. In search for substances suitable for this purpose, attention was paid to organic solvents used currently in iodometry, both water soluble and insoluble. Table 1 shows the effect of these wetting agents on the amount of the determined peroxides of PP oxidized for 40 min at 20°C during 5 h in the presence of HI (5 ml; concentration 7.58 mol l^{-1}). In each case 5 ml of wetting agent was used, which was enough for thorough wetting of 0.45 g of PP.

It is evident (Table 1) that the highest values of peroxides determined were obtained in the presence of wetting agents immiscible with water, mainly chloroform or its mixtures with *n*-heptane. *n*-Heptane is convenient because when added as the last component it enables a pure sealing of ampules.

These results led to investigations in the presence of chloroform and *n*-heptane at volume ratio 1 : 1. The expected three main factors affecting decomposition of polypropylene peroxides were examined, *viz.* HI concentration in the aqueous phase, temperature, and reaction time. Table 2 shows the effect of these factors on the amount of peroxides determined as well as on the results of polymerization in the presence of PP from which a part of peroxides was removed under the respective conditions.

The increasing values of peroxides determined and the decreasing conversions (Table 2) indicate the positive effect of an increase of HI concentration, tem-

Table 1

Effect of various wetting agents and their mixtures on the results of peroxide determination at 20°C during 5 h

Wetting agent	PP peroxides (mole O ₂ kg ⁻¹) · 10 ²
Chloroform	2.3
<i>n</i> -Heptane	1.9
Benzene	2.0
Isopropyl alcohol	1.8
Acetic anhydride	0.5
Glacial acetic acid	1.6
Chloroform : <i>n</i> -heptane = 4 : 1	2.3
Chloroform : <i>n</i> -heptane = 1 : 1	2.5
Chloroform : <i>n</i> -heptane = 1 : 4	2.0

Table 2

Effect of the HI concentration, temperature, and time of decomposition on the amount of peroxides determined and on the conversion of ST at 35°C in the presence of PP in which the peroxides were decomposed under the given conditions

HI mol l ⁻¹	Temperature °C	Time h	PP peroxides ^a (mol kg ⁻¹) · 10 ²	Bonded ST	Homopolymer
				%/3 h	
4	70	5	3.0	46.0	0.6
6	70	5	3.8	12.2	0.4
7.58	70	5	4.2	2.3	0.2
6	20	5	1.5	56.9	2.5
6	50	5	2.8	42.4	0.6
6	80	5	4.1	5.1	0.3
6	70	1	2.2	25.0	0.6
6	70	3	3.5	18.4	0.5
6	70	8	4.2	8.7	0.3
—	—	—	—	34.5	4.4

a) The system contained 0.45 g of PP oxidized for 40 min, 5 ml of HI solution, 2.5 ml of chloroform, and 2.5 ml of *n*-heptane; simultaneously an experiment was performed in the presence of unoxidized PP (30–50% of total consumption).

perature, and elongation of the reaction time necessary for decomposition of PP peroxides. Since the thermal decomposition of PP hydroperoxide begins at the temperatures above 30°C and the decomposition of more stable peroxide above 40°C, the values of the peroxidic content established at higher temperatures than those mentioned above are influenced by thermal decomposition of the peroxides which proceeds simultaneously. In this case, therefore, only the results of polymerization can be used to evaluate a measure of decomposition of isotactic powdered PP peroxides.

To define better the effects of factors presented in Table 2, designed experiments were performed enabling their complex evaluation. On this basis we considered only the values of the bonded monomer. We looked for the conditions of the minimal conversion which was regarded as a measure of quantitative decomposition of more stable peroxide groups of PP able to initiate this kind of polymerization in the given system.

On the basis of the previous experience and with the aim to approach these conditions, we examined the effect of the reaction temperature up to 90°C, reaction time of more than 8 h; the maximum HI concentration being limited by the composition of distilling azeotrope at atmospheric pressure. The individual levels of factors in the designed experiment assumed the values of the coded working variables x_1, x_2, x_3 in terms of demands of central composition rotatable design [8] according to Table 3.

The plan of the experiment (Table 4) consisted of the complete factor experiment of the type 2^3 (No. 1—8), axial points (No. 9—14), and the central zero points (No. 15—20) serving for the estimate of the experimental error for conversion determination. Samples No. 21—25 were used for additional independent verification of adequacy of the approximation regression relation. Apart from the conditions under which the PP peroxides decomposed, Table 4 presents also experimental results of the conversions of the bonded monomer obtained at 35°C during 3 h with PP deprived of peroxides (Y_{exp}) as well as the values of conversions assumed by regression (Y_{theor}).

From the results of parallel central experiments given in Table 4 (No. 15—20), the experimental variance of the conversion of bonded monomer, $S^2(y) = 0.097227$ with 5 degrees for freedom, was obtained corresponding to the experimental error $S(y) = \pm 0.31\%$.

Numerical evaluating of data from Table 4 afforded estimate regression coefficients of the approximation polynomial of the second degree in the coded form

$$Y = b_0 + \sum_{i=1}^3 b_i x_i + \sum_{\substack{i,j=1 \\ i < j}}^3 b_{ij} x_i x_j + \sum_{i=1}^3 b_{ii} x_i^2$$

The regression coefficients calculated and given with the corresponding standard deviations had the values

Table 3

Conditions of the experimental design

x_i	Factor	j Level of factor x_i					Interval I_i
		-1.682	-1	0	+1	+1.682	
x_1	Temperature, °C	49.8	58.0	70.0	82.0	90.2	12
x_2	HI, mol l ⁻¹	4.216	4.898	5.898	6.898	7.58	1.0
x_3	Time, min	98	180	300	420	502	120

Table 4

Basic data and results of the experimental design

No.	x_1	x_2	x_3	Bonded ST %/3 h	
				Y_{exp}	Y_{theor}
1	-1	-1	-1	59.43	60.47
2	+1	-1	-1	16.30	17.87
3	-1	+1	-1	13.16	13.49
4	+1	+1	-1	2.28	4.29
5	-1	-1	+1	48.68	48.12
6	+1	-1	+1	8.60	8.71
7	-1	+1	+1	8.71	8.62
8	+1	+1	+1	1.16	1.60
9	-1.682	0	0	42.18	41.87
10	+1.682	0	0	1.90	0.15
11	0	-1.682	0	46.06	45.49
12	0	+1.682	0	2.33	0.84
13	0	0	-1.682	25.18	22.35
14	0	0	+1.682	8.94	9.70
15	↑	↑	↑	12.69	12.56
16	↑	↑	↑	12.17	12.56
17	0	0	0	12.90	12.56
18				12.75	12.56
19	↓	↓	↓	12.20	12.56
20	↓	↓	↓	12.33	12.56
21	-1.682	+1.682	+1.682	7.00	6.71
22	-1	+1.682	-1.5	8.67	8.12
23	0	+1	+1	4.60	2.12
24	+1	0	0	5.07	3.15
25	+1.682	-1	-1	6.15	8.81

$$\begin{array}{l}
 b_0 = 12.561 \pm 0.127 \\
 b_1 = -12.403 \\
 b_2 = -13.272 \\
 b_3 = -3.759
 \end{array}
 \left. \vphantom{\begin{array}{l} b_0 \\ b_1 \\ b_2 \\ b_3 \end{array}} \right\} \pm 0.084
 \quad
 \begin{array}{l}
 b_{12} = +8.098 \\
 b_{13} = +0.798 \\
 b_{23} = +1.618
 \end{array}
 \left. \vphantom{\begin{array}{l} b_{12} \\ b_{13} \\ b_{23} \end{array}} \right\} \pm 0.110$$

$$\begin{array}{l}
 b_{11} = +2.987 \\
 b_{22} = +3.749 \\
 b_{33} = +1.225
 \end{array}
 \left. \vphantom{\begin{array}{l} b_{11} \\ b_{22} \\ b_{33} \end{array}} \right\} \pm 0.082$$

Table 4 shows to what extent the approximation regression equation describes real relations among the variables considered.

The data from Table 4 enable only qualitative evaluation of the truthfulness of the regression description of relations between the conditions of PP peroxides decomposition by HI and the resulting conversion of the bonded monomer. The difference between experimental and calculated data for conversion is on the average less than 2%.

To make the calculations complete, a regression analysis of all results was made (Table 5).

Results of the analysis given in Table 5 show that both linear and quadratic terms of the polynomial approximation are of great importance. The adequacy of equation is not guaranteed from the formal point of view on the basis of the F test. One can assume, however, that with respect to the multicomponent polymerization system used, especially in the presence of the solid phase of the oxidized PP, the estimate of the experimental error obtained is too low. The standard deviation of the estimate is according to the regression equation $S_R = \pm 1.5\%$ more probable under the given experimental conditions and can be regarded as a real statistical

Table 5

Complete regression analysis of the results of the design

Source of variability	S	f	s ²	F	F ^{crit}	
					0.05	0.01
$S_1 = \sum b_i(iy)$	4699.612868	3	1566.54		5.41	12.06
$S_2 = b_0(0y) + \sum b_{ij}(ijy) - (0y)^2/N$	857.893981	6	142.98		4.95	10.67
$S_{012} = b_0(0y) + \sum b_i(iy) + \sum b_{ij}(ijy)$	12035.706974	10	1203.57	very		
$(yy) = \sum y_u^2$	12059.5683	20		sig-		
$(0y)^2/N = (\sum y_u)^2/N$	6478.200125	1		nifi-		
$S_R = (yy) - S_{012}$	23.861326	10	2.386	cant	4.74	10.05
$S_E = \sum (y_{0u} - y_0)^2$	0.486133	5	0.097227			
$S_{LF} = S_R - S_E$	23.375193	5	4.675		5.05	10.97
$S_R = \pm 1.5\%$			$S_E = \pm 0.31\%$			

estimate of the experimental error. Regardless of the results of the analysis (Table 5), the polynomial with the given regression coefficients can be used for approximating the real relations among variables with the estimate error $\pm 1.5\%$ (for 68% probability) in the form

$$Y = 12.561 - 12.403 x_1 - 13.272 x_2 - 3.759 x_3 + 8.098 x_1 x_2 + 0.798 x_1 x_3 + 1.618 x_2 x_3 + 2.987 x_1^2 + 3.749 x_2^2 + 1.225 x_3^2 \quad (1)$$

Many regression coefficients (10) and thus also complicated equation do not afford any idea about the effects of the basic three factors. More information can be obtained by further rearrangement of the original eqn (1) corresponding to the canonical form

$$Y - 0.987 = 7.554 X_1^2 - 0.730 X_2^2 + 1.130 X_3^2 \quad (2)$$

On the basis of eqn (2) with the centre of symmetry (stationary point)

$$\begin{aligned} x_{1s} &= +0.462 \\ x_{2s} &= +1.134 \\ x_{3s} &= +0.635 \end{aligned}$$

and conversion in this point

$$Y_s = +0.987$$

at least preliminary estimate of the form of functional dependence can be done. The real experimental space has four dimensions, therefore graphical representation of the hypersurface (conversion) is beyond the limits of the ideas about forms. In each case it can be said on the basis of regression considerations that the hypersurface dependent on the three basic conditions of PP peroxide decomposition represents a quadric of the hyperbolic paraboloid type ("saddle" hypersurface).

These rather complicated ideas were later simplified by diminishing the dimension of the experimental space when one variable was chosen as constant. For each level of this factor regression equations of the second degree and their corresponding canonical forms were obtained in this way. On this basis contour diagrams were constructed, describing illustratively and quantitatively three-dimensional relations among the variables considered.

Of three possible simplifications, only one was employed for the interpretation of the results, *viz.* dependence of conversion on the HI concentration and the time of its action as a parameter for the reaction temperature. For temperatures given in Table 3, regression coefficients b for the dependence of conversion on the given two factors were calculated (Table 6); index 2 refers to HI concentration, index 3 to the reaction time

$$Y = b_0 + b_2 x_2 + b_3 x_3 + b_{23} x_2 x_3 + b_{22} x_2^2 + b_{33} x_3^2$$

Table 6

Regression coefficients of equations for various temperatures

Temperature		b_0	b_2	b_3	b_{23}	b_{22}	b_{33}
x_1	$^{\circ}\text{C}$						
-1.682	49.8	41.873	-26.896	-5.101	↑	↑	↑
-1.000	58.0	27.951	-21.370	-4.557			
0.000	70.0	12.561	-13.272	-3.759	+1.618	+3.749	+1.225
+1.000	82.0	3.145	-5.174	-2.961	↓	↓	↓
+1.682	90.2	0.150	+0.349	-2.417			

The corresponding canonical forms of equations as well as necessary characteristics of orthogonal transformation of ordinates were obtained (Table 6). Calculations gave a good idea of the effects of all three factors through contour diagrams as shown in Figs. 1—5. Experimental points are denoted as circles with % of conversion in brackets. The data at isolines are % of conversion assumed by regression.

Contour diagrams (Figs. 1—5) indicate that mutual relations of the quantities considered in the space are represented by the elliptical paraboloid with unambiguous minimum.

The minimum of the styrene conversion is shifted to higher HI concentrations with decreasing reaction temperature: while at 90.2 $^{\circ}\text{C}$ (Fig. 1) it lies at $[\text{HI}] = 5.5$,

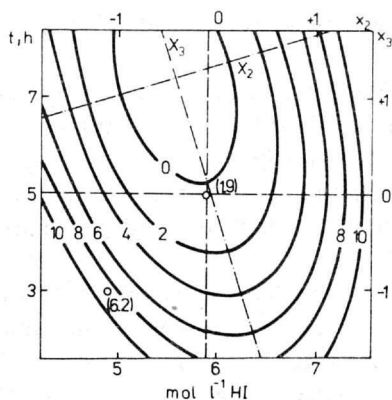


Fig. 1. Contour diagram of the dependence of bonded styrene amount (%) on PP at 30 $^{\circ}\text{C}$ for 3 h on HI concentration and time of action of the decomposition system at 90.2 $^{\circ}\text{C}$.

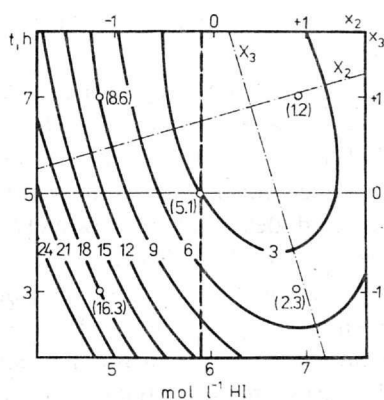


Fig. 2. Contour diagram of the dependence of bonded styrene amount (%) on PP at 30 $^{\circ}\text{C}$ for 3 h on HI concentration and time of action of the decomposition system at 82 $^{\circ}\text{C}$.

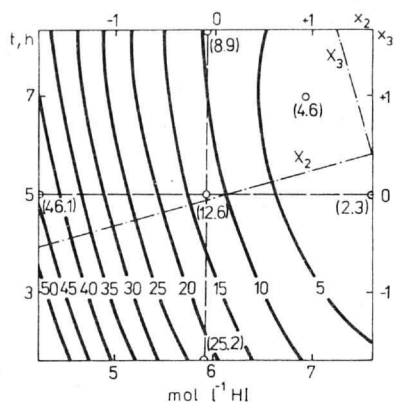


Fig. 3. Contour diagram of the dependence of bonded styrene amount (%) on PP at 30°C for 3 h on HI concentration and time of action of the decomposition system at 70°C.

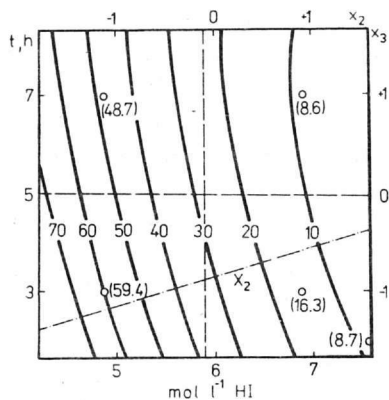


Fig. 4. Contour diagram of the dependence of bonded styrene amount (%) on PP at 30°C for 3 h on HI concentration and time of action of the decomposition system at 58°C.

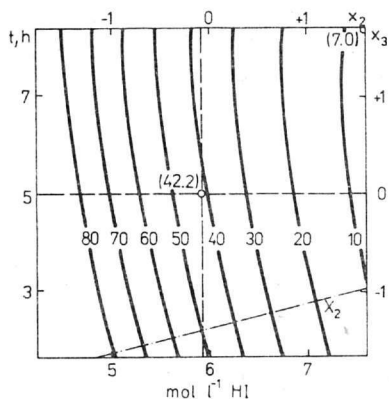


Fig. 5. Contour diagram of the dependence of bonded styrene amount (%) on PP at 30°C for 3 h on HI concentration and time of action of the decomposition system at 49.8°C.

at 82°C (Fig. 2) at $[HI] = 6.5$, and at 70°C (Fig. 3) it is on the border of the maximum attainable HI concentration; at lower temperatures (Figs. 4 and 5), the minimum of polymer formation does not lie in the experimental region any more and can be expected only at unreally high HI concentrations. The effect of the time of the action of HI becomes more marked with increasing temperature: the real times of 6–7 h necessary for the minimum conversion are reached at 70°C and higher temperatures, at lower temperatures even its great prolongation would not yield desirable result.

The complex analysis of the conditions for the decomposition of peroxides of isotactic powdered PP able to initiate polymerization in the given system shows

unambiguously that the required decomposition activity of HI with respect to these peroxides is conditioned by simultaneous use of the relatively high reaction temperatures, 70°C and higher; this being in agreement with the known facts [6, 7]. However, in this connection it can be stated that regarding the considerable thermal lability of the peroxides, the method cannot be employed for their quantitative determination. For this purpose it will be necessary to look for more active decomposition agents which would allow for the temperature decrease during their decomposition.

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Translated by P. Ambrovič