

Iodometric determination of hydroperoxides of powdered isotactic polypropylene

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Dedicated to Professor RNDr J. Gašperík on his 70th birthday

On the basis of experimental designing and statistical analysis a iodometric method for selective determination of hydroperoxides of powdered isotactic polypropylene at 20°C has been worked out. In the elaboration of this the properties of oxidized polypropylene as a macromolecular initiator for styrene polymerization in emulsion activated by Fe^{2+} —triethylenetetramine chelate have been utilized.

Методом планированного эксперимента и его статистической оценкой разработана иодометрическая система для селективного определения гидроперекисей изотактического порошкового полипропилена при 20°C. При разработке методики определения использовались свойства окисленного полипропилена как высокомолекулярного инициатора полимеризации стирола в эмульсионной системе активированной внутрикомплексным соединением Fe^{2+} —триэтилентетрамин.

There are usually no problems with an analytical determination of peroxides in polymers soluble at low temperatures; complications arise if the polymer is insoluble or soluble at temperatures, at which simultaneously a thermal decomposition of the studied peroxides occurs. The presence of a solid phase often makes it impossible to use some of the routine physical method for peroxide determination. Owing to fact that the peroxide concentration is usually low and their quantitative determination in heterogeneous system is frequently distorted by adsorption effects, it is necessary to check the correctness of determination by some other method [1]. These problems can occur also in the case of oxidized powdered isotactic polypropylene.

Peroxides of powdered isotactic polypropylene have been successfully used as initiation centres for emulsion polymerization of styrene in the presence of an activator, particularly chelate FeSO_4 —triethylenetetramine, at low temperature [2, 3], whereupon bonding of the polymer on polypropylene occurred and a small amount of homopolymer was formed. It was found out [4] that the most reactive peroxides of polypropylene — the hydroperoxides — initiate formation of homopolymer and simultaneously they have negative influence on the modification of polypropylene. In dependence upon the extent of their removal from

polypropylene the amount of bonded polymer is increased while the homopolymerization rate simultaneously decreases [5].

In this paper a convenient composition of the system for hydroperoxide determination of powdered isotactic polypropylene was studied by means of experimental designing and mathematical analysis. The accuracy degree and selectivity of the determination was checked with respect to the results of styrene polymerization, initiated by peroxides of polypropylene. The iodometry is used as the determination method, because it has several advantages in comparison with other methods for peroxide determination in the presence of a solid phase of powdered isotactic polypropylene [6].

Experimental

Chemicals

Polypropylene (PP) — powdered, produced by Slovnaft, Bratislava, with following characteristics:

Atactic portion	0.4%
Stereoblocks	3.1%
Ashes	0.14%
Viscosity	376.0 ml/g
Bulk weight	108.0 g/l

The residual atactic portions and the stereoblocks were removed from polypropylene by extraction with *n*-heptane. A polymer with a granularity of 0.10—0.15 mm was used.

Styrene (ST) was purified of stabilizer by shaking with a 10% solution of aqueous NaOH, dried with CaCl₂ and twice distilled in a nitrogen atmosphere.

Triethylenetetramine was synthesized from ethylenediamine and ethylene dichloride [7] and was used as an aqueous solution.

FeSO₄ anal. grade was used as an aqueous solution and acidified by H₂SO₄ to pH 5.5.

Emulsifier, Mersol H, was produced by Leuna Werke (GDR). The average composition was CH₃—(CH₂)₁₆—SO₃Na, it was used as an aqueous solution.

All solutions were prepared using water distilled from glass and boiled under nitrogen. The solutions were stored in a nitrogen atmosphere.

Traces of oxygen were removed from nitrogen by passing through a column containing a filling of the composition 55% MnO₄, 40% MgO, and 5% Cr₂O₃ at room temperature.

Other chemicals (chloroform, carbon tetrachloride, isopropyl alcohol, benzene, *n*-heptane, glacial acetic acid, KI, NaI, Na₂S₂O₃ and starch) were anal. grade.

Procedures

Polypropylene was oxidized by means of a fluidization method over 40 min by oxygen with an ozone content of 12 mg O₃/l at room temperature.

Hydroperoxides in polypropylene were determined as follows: 0.45 g of powdered isotactic polypropylene was evacuated in ampules and the vacuum was succeeded by nitrogen. The liquid components of the decomposition system (wetting agents, glacial acetic acid, and saturated aqueous KI solution) were added in a nitrogen atmosphere, then 30 min bubbled with nitrogen with a total volume 10—15 ml. In other cases KI was added in a solid form to polypropylene before the evacuation. After sealing, the ampules were located on a revolving frame in a tempered bath at 20°C. After 5 hrs of the

reaction liberated iod was determined by $\text{Na}_2\text{S}_2\text{O}_3$ with a starch indicator. The content of hydroperoxides in polypropylene was expressed in moles of active oxygen in kg of polypropylene (mole O, kg). During the procedure an experiment in the presence of nonoxidized polypropylene was made which value, if using sufficiently pure chemicals was usually zero. In those cases, where polypropylene after determination of hydroperoxides was used in the polymerization system, the residues of the iodometric decomposition system were removed from the polymer by washing with a mixture acetone—water, and with acetone and then vacuum dried at room temperature. The sample required for the polymerization (0.5 g) was obtained from the two parallel determinations.

The polymerization procedure has been described previously [8]. The polymerization system consisted of a solid phase containing 0.5 g of polypropylene oxidized for 40 min and of a liquid phase (total volume 15 ml) in which FeSO_4 (1.33×10^{-3} mole/l aqueous phase), triethylenetetramine (2.00×10^{-3} mole/l aqueous phase), and emulsifier (9.75×10^{-3} mole/l aqueous phase) were dissolved, and of an organic phase represented by styrene (3 ml). After 3 or 5 hrs of polymerization at 30°C , solid phase containing modified polypropylene was recovered on a sintered glass and from the emulsion which passed the sintered glass, the nonbonded homopolymer was precipitated by methanol. In both cases the conversion was expressed in % of reacted styrene with respect to the initial amount (% of bonded ST or % homopolymer).

Results and discussion

The thermal stability of hydroperoxides of powdered isotactic polypropylene is relatively low (an appreciable decomposition occurs already at temperatures above 30°C [4]), therefore no attempts were made to dissolve polypropylene. The attention was focused only on the determination of those peroxides of polypropylene which were able to initiate polymerization.

In the elaboration of the procedure for determination of the above peroxides experience acquired in iodometric determination of hydroperoxides in masticated natural rubber [9] has been utilized. In the case of polypropylene the used organic solvents took over the role of a wetting agent permitting the contact of the reacting compounds with the polypropylene surface. Upon looking for suitable compounds for this purpose, the attention was drawn to the solvents frequently used in the iodometry. The results of the study of the influence of various wetting agents of polypropylene and of their mixtures in the presence of glacial acetic acid and KI at 20°C on the amount of determined hydroperoxides are given in Table 1.

The results presented in Table 1 allow for following conclusions:

1. According to the results of hydroperoxide determination in polypropylene, the presence of auxiliary organic compounds in the system is necessary; a simplification of the system to only glacial acetic acid—KI has an unfavourable effect (sample 6).

2. From among the studied organic solvents chloroform should be preferred (sample 1); its mixture with *n*-heptane does not decrease the activity of the system (sample 7) and the presence of *n*-heptane added as the last component permits a pure sealing of the ampule.

3. The decomposition activity of the system is increased by the elimination of

Table 1

Influence of the composition of the iodometric system on the results of hydroperoxide determination of polypropylene oxidized for 40 min at 20°C over 5 hrs and on the amount of polymer formed during the polymerization in the presence of thus treated polypropylene at 30°C over 3 hrs

No.	Components (ml) ^a					Glacial acetic acid	Hydroperoxides of PP ($\frac{\text{mole O}_2}{\text{kg}}$) 10 ²	Bonded ST (%/3 hrs)	Homopolymer (%/3 hrs)
	Chloroform	Carbon tetra-chloride	<i>n</i> -Heptane	Benzene	Isopropyl alcohol				
1	5					10	1.0	33.2	2.0
2		5				10	0.9	32.4	2.1
3			5			10	0.3	26.6	3.6
4				5		10	0.7	30.2	2.5
5					5	10	0.1	25.0	4.5
6						15	0.1	24.8	4.6
7	2.5		2.5			10	1.0	33.6	1.9
8		2.5	2.5			10	0.6	29.2	2.7
9 ^b	2.5		2.5			10	1.5	38.1	1.5
10 ^b						15	0.4	27.4	3.3
11 ^c	2.5		2.5			10	0.9	32.6	2.0
12 ^d							—	23.8	4.9

a) The system contained 0.45 g of polypropylene oxidized for 40 min and 2 ml of saturated aqueous KI solution; decomposition time 5 hrs.

b) 0.5 g KI was used.

c) 2 ml of a saturated NaI solution was used.

d) The original sample of oxidized polypropylene.

water by adding solid KI (samples 7 and 9, 6 and 10); the application of NaI has not a favourable effect (samples 7 and 11).

4. The data on polymer formation in the presence of polypropylene from which in advance the hydroperoxides were removed by one of the iodometric methods prove that the deeper was the decomposition the lower was the amount of the homopolymer formed and the higher was the conversion of the bonded styrene, this being in agreement with the previously observed positive influence of hydroperoxide removal on the formation of the copolymer and with the negative influence of homopolymer formation [4]. Compared with the reference sample 12 these values of conversions particularly in the case of more expressive conversions of styrene bonding reflex sensitively every concentration change of hydroperoxides of polypropylene used in the polymerization system and may serve as a quantitative measure for hydroperoxide removal from polypropylene.

The procedure for checking the presence of hydroperoxide groups in polypropylene based on polymerization results proposed in point 4 makes a choice possible of conditions for a selective determination of hydroperoxides of polypropylene in the presence of more stable peroxides of polypropylene which initiate the formation of copolymer in the given polymerization system. From the values obtained by the iodometric determination it is namely not clear whether the hydroperoxides were determined quantitatively and, on the other hand, if beside hydroperoxides a part of more stable peroxides of polypropylene was not determined simultaneously. This approach to the appreciation of the results of iodometric determination of hydroperoxides can be estimated on the basis of values presented in Table 2 which were obtained in the study of the temperature influence on the determination of hydroperoxides of polypropylene (further only results of the modification of polypropylene are presented; the polymerization time was

Table 2

Influence of temperature on the amount of determined peroxides over 5 hrs in polypropylene oxidized for 40 min and on the polymerization results at 30°C over 5 hrs, in the presence of thus treated polypropylene

No.	Temperature °C	Peroxides of PP* (mole O ₂ /kg) · 10 ²	Bonded ST (%/5 hrs)
1	10	1.3	60.5
2	20	1.5	62.5
3	30	1.7	60.0
4	40	1.9	40.5
5	50	2.1	17.0

* The decomposition system: 0.45 g 40 min oxidized PP, 10 ml glacial acetic acid, 2.5 ml chloroform, 2.5 ml *n*-heptane, 0.5 g KI, decomposition time 5 hrs.

extended up to 5 hrs in order to make more expressive the differences of the conversion values).

It is unambiguously evident from Table 2 that the temperatures above 30°C are not suitable for a selective determination of hydroperoxides of polypropylene; from the polymerization results it is evident that at higher temperatures the determined value includes also that portion of polypropylene peroxides, from which the copolymer is produced, this being proved by a significant decrease of the copolymer formation observed already at 40°C. For the determination of hydroperoxides alone lower temperatures (close to 20°C) are suitable. By change of the conversion of bonded styrene it is then possible to estimate simultaneously the concentration changes of both assumed kinds of polypropylene peroxides.

Thus it was possible to proceed to a more detailed study of the composition of the iodometric system suitable for a selective determination of hydroperoxides of powdered isotactic polypropylene. On the basis of the results presented in Tables 1 and 2 a decomposition system consisting of glacial acetic acid, chloroform, *n*-heptane, and solid KI was chosen for this investigation. The working temperature was 20°C. As this was a multicomponent system, the experimental design was used for choosing the mutual proportions of components. On the basis of the previous experience, as a measure for a quantitative and selective removal of hydroperoxide groups from polypropylene such conditions have been looked for at which the highest amount of bonded styrene was formed.

The experimental orthogonal design of the second order which was used in this work has been described previously [10]. It is a two-factorial experiment on three levels. As the first factor the volume ratio of glacial acetic acid to the organic phase, represented by the volume of chloroform and *n*-heptane (OCT : OF), was chosen; the second factor was the volume ratio of chloroform and *n*-heptane in the organic phase (CHL : HE). The total volume of the liquid components for 0.45 g of polypropylene oxidized for 40 min was adjusted to 10 ml which enabled for a good motion of the reacting mixture in the ampule, and 0.5 g KI was added. The decomposition time of hydroperoxides was 5 hrs at 20°C, the time of polymerization by using treated polypropylene samples was 5 hrs at 30°C. The chosen levels of the experimental design are presented in Table 3.

Table 3

Conditions of the experimental design

x_i	Factor	Factor level			Interval I_i
		-1	0	+1	
x_1	OCT : OF	1.5	6.5	11.5	5
x_2	CHL : HE	1.0	2.0	3.0	1

According to the requirements of the orthogonal design 9 basic experiments were made. The results are summarized in Table 4 together with the theoretical results assumed regressively.

Table 4

Basic data and results of the experimental design				
	x_1	x_2	Bonded ST (%/5 hrs)	
			Y_{exp}	Y_{theor}
1	-1	-1	66.0	66.6
2	-1	0	67.0	66.0
3	-1	1	67.7	68.1
4	0	-1	65.9	65.5
5	0	0	64.5	65.0
6	0	1	67.2	67.2
7	1	-1	61.7	61.6
8	1	0	60.7	61.2
9	1	1	63.8	63.5

The experimental standard error of the conversion of styrene bonding estimated from parallel determinations was found to be $\pm 1.4\%$.

On the basis of values presented in Table 4 by a routine calculation procedure an equation describing the relation among the yield of bonded styrene (Y) and the parameters x_1 and x_2 was derived

$$Y = 64.98 - 2.42x_1 + 0.85x_2 + 0.10x_1x_2 - 1.38x_1^2 + 1.32x_2^2 \quad (1)$$

The eqn (1) can be rearranged into a canonical form

$$Y - 65.93 = 1.32x_1^2 - 1.38x_2^2 \quad (2)$$

Comparing the experimental results with the regressively estimated ones it is possible to verify their excellent agreement.

The eqn (2) represents a hyperbolic paraboloid ("saddle"), with approximately the same slope in both ascending and descending directions of the canonical axis. However, in the whole experimental space the conversion change of bonded styrene is not very expressed with respect to the estimated value of the standard error.

It is possible to illustrate the functional relation (1) or (2) graphically by a contour diagram of the conversion of bonded styrene in dependence on the ratio of glacial acetic acid to the organic phase and on the ratio of chloroform to *n*-heptane (Fig. 1).

From the results shown in Fig. 1 it follows that an increase of the conversion of

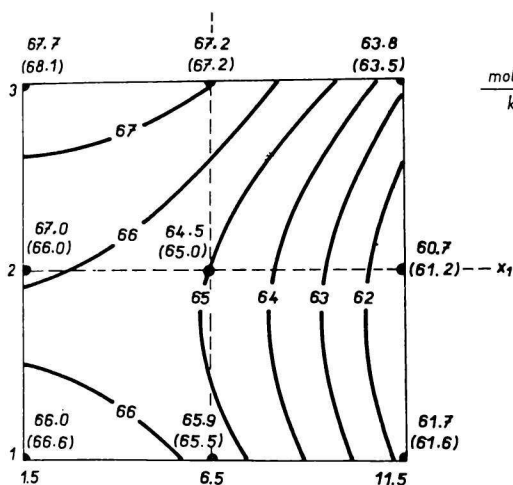


Fig. 1. Contour diagram of dependence of conversion of styrene bonding over 5 hrs at 30°C on the ratio of glacial acetic acid to organic phase (x_1) and on the ratio of chloroform to *n*-heptane (x_2) in the iodometric decomposition system. The experimental values are marked by full circles with a numerical value of conversion over 5 hrs in %. The numerical values in brackets are conversions assumed regressively. The numerical values at the isolines represent conversion over 5 hrs in % assumed regressively.

bonded styrene can be expected only in the area of the lower ratio of glacial acetic acid to the organic phase and simultaneously it seems to be more advantageous to work with a higher ratio of chloroform to *n*-heptane. This finding has been confirmed by a series of supplementary experiments outside of the experimental area where the ratio of glacial acetic acid to organic phase was less than 1.5 and the ratio of chloroform to *n*-heptane higher than 3. The results are presented in Table 5. These results prove that a farther decrease of glacial acetic acid content and a contingent omission of *n*-heptane from the system for determination of polypropylene hydroperoxides have no positive influence on the yield of copolymer. Hence it was assumed that in this case does not exist an actual optimum for copolymer formation and that in a relatively wide area of the volume ratios of glacial acetic acid to organic phase and the volume ratios of chloroform to *n*-heptane it is possible to obtain maximum conversions of 67 to 68% over 5 hrs.

On the basis of an analysis of the above results a iodometric decomposition system was proposed for a selective determination of hydroperoxides of oxidized isotactic polypropylene with the ratio OCT:OF=1:1 and CHL:HE=4:1 which means that the system with an initial weight of 0.45 g of polypropylene

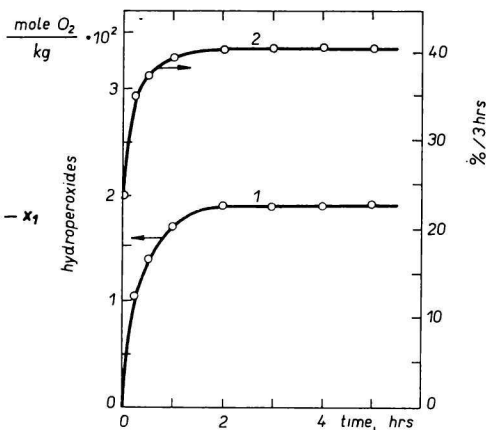


Fig. 2. Influence of the duration of treatment by the iodometric decomposition system at 20°C on the amount of determined hydroperoxides of polypropylene oxidized for 40 min (1) and on the amount of bonded styrene over 3 hrs of polymerization at 30°C using polypropylene which was for the corresponding time in contact with the iodometric decomposition system (2).

Table 5

Check points of the influence of factor levels outside of the experimental area

No.	OCT : OF	CHL : HE	Bonded ST (%/5 hrs)
1	0.1	6	66.0
2	0.1	10	64.7
3	0.5	6	67.3
4	0.5	10	67.2
5	0.75	6	67.1
6	0.75	10	66.7
7	0.75	∞	66.0

contains 5 ml of glacial acetic acid, 4 ml of chloroform and 1 ml of *n*-heptane in the presence of 0.5 g KI; the reaction temperature is 20°C and the reaction time is 5 hrs.

The kinetics of polypropylene hydroperoxide decomposition was studied using the mentioned iodometric system and it was found (Fig. 2, curve 1) that the rate of this reaction is relatively high which makes it possible to shorten substantially the time required for the determination without influencing the results. This conclusion is confirmed by the values of conversion of bonded styrene (curve 2) in the presence of polypropylene which was for the corresponding time in contact with the iodometric system.

The standard error of determination of hydroperoxides of powdered isotactic polypropylene by the mentioned iodometric methods was found to be ± 0.037 mole O₂/kg, which means for hydroperoxides of polypropylene oxidized for 40 min less than 2% relatively.

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