

PARAMAGNETISM OF CARBONIZATION PRODUCTS FORMED FROM ISOTACTIC POLYPROPYLENE CONTAINING SYNTHETIC ZEOLITES

Josef RYCHLÝ, Lydia MATISOVÁ-RYCHLÁ and Ján PLAČEK

*Institute of Polymers,
Slovak Academy of Sciences, 809 34 Bratislava*

Received July 18th, 1977

The paramagnetism was studied of products obtained by the carbonization of isotactic polypropylene with synthetic zeolites NH_4Y and NiY and their mixtures with ammonium phosphate, N-bromosuccinimide and dibenzoyl peroxide. The interpretation of ESR signals in carbonized samples is based on the existence of stable carbenes. In the case of synergistic mixtures of flame retardants such as ammonium phosphate, N-bromosuccinimide and dibenzoyl peroxide in polypropylene the increased rate of polymer oxidation is observed at 190°C which may be attributed mainly to the presence of ammonium phosphate.

A considerable attention has recently been devoted to ESR studies of products formed during the carbonization of organic substances. According to the latest hypotheses the paramagnetism of carbonization products is attributed to the collective interaction of conjugated bonds present in these organic systems^{1,2}. Also the presence of ferromagnetic substances seems to offer a plausible explanation of the observed paramagnetism³.

We have observed neither carbonization nor paramagnetism of isotactic polypropylene subjected to pyrolysis at c. 400°C in air. When, however, synthetic zeolites NH_4Y , MgY or compounds with acid catalytic centres are added to the polymer then a strong ESR signal is observed under similar pyrolytic conditions. If the presence of some inorganic material causes the formation of paramagnetic centres in the carbonized residue then the mechanism of their formation will be connected with the properties of the additive and *vice versa*.

In this paper we describe experiments in which the influence was examined of synthetic zeolites NH_4Y and NiY , resp., ammonium phosphate, benzoyl peroxide and N-bromosuccinimide as well as their various mixtures with isotactic polypropylene upon the paramagnetism of pyrolytic products. Moreover, the chemiluminescence of the system investigated was followed. A possible mechanism of the process is discussed as well as a connection with the processes of polypropylene burning or flame retardation.

EXPERIMENTAL

Powdered isotactic polypropylene, a product of Slovnaft Bratislava, was purified by a 3 times repeated extraction with hexane. Powdered synthetic zeolites NH_4Y and NiY were prepared

in Research Institute of Petroleum and Coal Products, Bratislava. The NH_4Y zeolite contained 8% NH_3 while the NiY type contained 10% NiO. The synthetic zeolites were used without previous activation. N-Bromosuccinimide of analytical grade was a Fluka AG Buchs product. Dibenzoyl peroxide was purified by recrystallisation from chloroform solution. Ammonium phosphate was of analytical purity.

Mixtures of synthetic zeolites with polypropylene were prepared in a ball-homogenizer, the zeolite contents being 10%. The mixtures were then pyrolysed at selected temperature in air for 10 minutes. After the end of pyrolysis and cooling down the sample the concentration of paramagnetic particles was determined by means of the ESR method. For this purpose an X-band spectrometer Varian E-4 was used, the microwave power being 10 mW and modulation amplitude 0.2 mT. The ESR spectra exhibited a singlet. The concentration of paramagnetic particles was determined in arbitrary units as $c = h \cdot (\Delta H)^2 / m \cdot s$, where h is peak height in cm, ΔH represents its width in mT, m stands for the weight of sample in mg, s being the sensitivity setting. The intensity of the observed line slightly decreases in the presence of oxygen (c. 20% per hour).

The samples of IPP with additives for chemiluminescence measurements were prepared by the homogenization of IPP, ammonium phosphate, dibenzoyl peroxide and N-bromosuccinimide in a ball-homogenizer for 2 minutes at ambient temperature. 100 mg samples were taken for each measurements. The measurements were carried out in air at temperature 190°C *i.e.* at temperature of sample melting. A PU SNK 7M spectrometer made in the Institute of Chemical Physics, Soviet Academy of Sciences, Moscow, was employed for the measurements; the instrument is equipped with a FEU-38 photomultiplier whose photocathode has maximum spectral response at 460 nm. The chemiluminescence intensity was expressed in relative units; one relative unit corresponds to current of $1.4 \cdot 10^{-13}$ amperes, the resistance setting being $1 \cdot 10^{11} \Omega$.

RESULTS

The concentration of paramagnetic particles in the carbonized residue of the system NH_4Y -isotactic polypropylene (iPP) is changing with temperature, the maximum

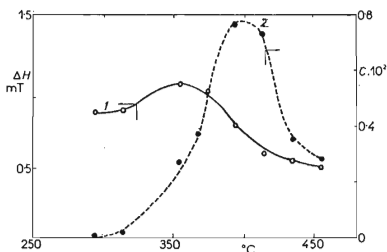


FIG. 1

The Temperature Dependence of Paramagnetic Signal Intensity (c) and Line Width (ΔH) for the System Containing iPP- NH_4Y Pyrolysed for 10 Minutes in Air

TABLE I

The Dependence of Concentration of Paramagnetic Species in Carbonized iPP-NH₄Y Systems in the Presence of Dibenzoyl Peroxide (I), N-Bromosuccinimide (II) and Ammonium Phosphate (III) at 400°C

Symbols: For the definition see Experimental.

<i>m</i> mg	<i>I</i>	<i>II</i> %	<i>III</i>	<i>h</i> cm	ΔH mT	$s \cdot 10^{-2}$	$c \cdot 10^2$ arbitrary units
2.5	—	—	—	20.6	0.70	2.5	1.615
3.0 ^a	—	—	—	17.1	0.75	1.6	2.004
1.2 ^b	—	—	—	15.8	0.662	4.0	1.445
1.7	—	—	3.0	8.7	0.437	2.5	0.392
3.0	—	—	7.2	16.5	0.237	2.5	0.124
3.2	—	—	12.6	13.0	0.275	3.2	0.096
5.0 ^c	—	—	25.5	6.6	0.200	3.2	0.017
8.0	—	—	47.5	16.1	0.237	3.2	0.035
2.5	6.6	—	—	7.2	1.025	8.0	0.411
8.0	—	5.7	—	14.2	0.812	3.2	0.366
4.8	4.2	3.7	20.9	8.1	0.350	3.2	0.065

^a Another amount of ammonium phosphate added after the end of pyrolysis. ^b Paramagnetism of sample^a. ^c The sample pyrolysed in the absence of zeolite.

TABLE II

The Dependence of Concentration of Paramagnetic Species During the Carbonization of iPP-NiY Mixture at 400°C

$c_{Ni^0} = h(\Delta H)^2/m \cdot s$; For symbols definition see Experimental. *III* stands for ammonium phosphate.

<i>m</i> mg	<i>III</i> %	<i>h</i> cm	ΔH mT	$s \cdot 10^{-2}$	c_{Ni^0} arbitrary units	$c \cdot 10^2$ arbitrary units
4.6	—	2.8	76.0	2.5	14.1	0.165
7.2	—	6.0	75.5	1.6	29.7	—
2.4	1.3	14.1	76.0	1.6	212.1	—
4.0	7.5	14.2	76.0	1.6	128.2	0.026
8.0	10.8	14.3	77.0	1.0	105.9	0.022
9.2	23.5	17.3	77.0	1.6	69.6	0.010

being at 400°C. The singlet peak width in the ESR spectrum within the interval of 295–355°C is increasing at first, reaching the maximum at 355°C and then decreases. The maximum value of concentration of paramagnetic particles is reached approximately at the temperature which is almost the same as that of maximum narrowing of the ESR peak (Fig. 1).

The systems iPP-NH₄Y were then carbonized in air at 400°C and the influence of additives on the concentration of paramagnetic species (ammonium phosphate, N-bromosuccinimide NBS, dibenzoyl peroxide BP) was followed. These additives may form a synergistic mixture of flame retardants (Table I). The increasing concentration of phosphate in the system suppresses not only the concentration of paramagnetic species in the residue but causes also the singlet line narrowing in ESR spectra (from *c.* 0.7 mT to 0.2 mT). The additions of N-bromosuccinimide and dibenzoyl peroxide also lower the ESR signal intensity. The line-width, however, is increasing up to 1.0 mT in the case of N-bromosuccinimide. The mixture of all three above mentioned additives with iPP-NH₄Y is at given concentrations self-extinguishing. The decrease in intensity of ESR spectra is most pronounced in the case of phosphate while NBS and BP cause only a slight line broadening.

After taking ESR spectrum the carbonized sample was mixed with another 10 mg of ammonium phosphate and subjected to pyrolysis for another 8 minutes at 400°C.

The paramagnetic signal line obtained by measuring the system phosphate-iPP in the absence of NH₄Y zeolite exhibits 0.2 mT line width and intensity 0.017 · 10⁻² arbitrary units (25.5% of phosphate in the system).

The mixture of NiY with iPP exhibits an ESR spectrum in which Ni²⁺ species predominate and, the sample is ferromagnetic (Fig. 2). The signal corresponding to the carbonized residue is less intense – as much as by an order of magnitude when compared to the measurements in the presence of NH₄Y zeolite (Table II). A small amount of phosphate considerably enhances the formation of Ni²⁺; when

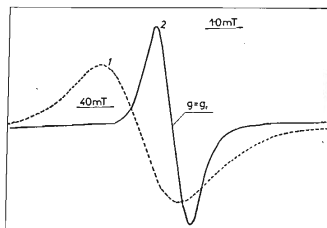


FIG. 2
ESR Spectrum of Ni²⁺-Particles Obtained Upon the Pyrolysis of System Containing iPP-NiY-Ammonium Phosphate at 400°C (1), and ESR Spectrum of Carbonized Products of System Containing iPP-NH₄Y after Pyrolysis at 400°C (2)

the concentration of phosphate in the mixture is increasing the concentration of Ni^{2+} steadily decreases (Fig. 3).

Fig. 4 compares time dependence of chemiluminescence intensity with pure isotactic polypropylene with systems containing additions of phosphates, dibenzoyl peroxide or N-bromosuccinimide. After the initial sharp peak the chemiluminescence intensity steadily increases reaching a stationary level after 15–20 minutes. This level decreases only slightly with time and it is a measure of the rate of sample oxidation. The initial peak which may be eliminated with a suitable composition of the mixture

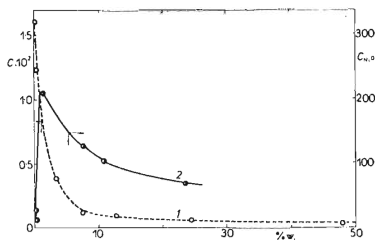


FIG. 3

The Phosphate Dependence of Concentration of Paramagnetic Particles c for System $\text{iPP-NH}_4\text{Y}$ -Ammonium Phosphate after Pyrolysis at 400°C (1); the Dependence of Ni^{2+} Concentration upon Phosphate Content in the System iPP-NiY -Ammonium Phosphate after Pyrolysis at 400°C (2)

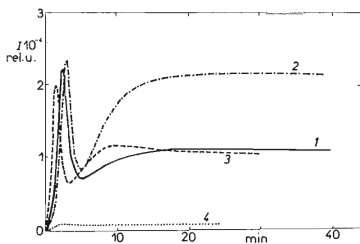


FIG. 4

Chemiluminescence Intensity at 190°C

Systems: 1 iPP , 2 iPP -Ammonium Phosphate (18.3%), 3 iPP -Dibenzoyl Peroxide (1.8%), 4 iPP -N-bromosuccinimide (5.5%).

TABLE III

The Dependence of Chemiluminescence Intensity Upon the Composition of the Mixture Containing IPP, Ammonium Phosphate, BP, NBS at 190°C

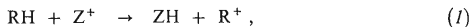
Overall weight 100 mg. Formulae of I—III explained in Table I.

	I	II	III	I_{max}	I_{stat}	\bar{I}_{stat}
	%			rel. units		
	—	—	—	24 000	11 000	
	—	—	—	22 600	11 200	11 400
	—	—	—	20 500	12 000	
	—	1·8	—	21 000	12 400	
	—	1·8	—	20 500	10 600	10 750
	—	1·8	—	19 000	10 000	
	—	1·8	—	21 500	10 000	
	—	—	—	16 600	10 000	
	—	0·8	—	15 400	9 200	9 100
	—	—	—	13 900	8 200	
	—	—	—	28 800	21 000	
10·9	—	—	—	27 000	23 000	20 600
	—	—	—	23 400	18 000	
	—	—	—	23 000	21 800	
	—	—	—	21 000	24 000	22 400
18·3	—	—	—	19 000	22 500	
	—	—	—	23 000	21 300	
	—	—	1·8	2 000	4 600	
	—	—	—	2 000	5 200	4 900
	—	—	5·5	900	800	850
	—	1·0	1·8	8 600	6 500	6 550
	—	—	—	7 800	6 600	
	—	—	—	10 000	20 400	
10·2	0·9	—	—	10 800	21 000	21 000
	—	—	—	9 500	21 500	
	—	—	—	5 500	16 500	
10·1	—	—	1·7	5 400	18 000	16 800
	—	—	—	5 300	16 000	
12·6	3·4	—	—	18 000	19 600	20 550
	—	—	—	12 000	21 500	
	—	—	—	—	23 000	
10·6	0·7	1·8	—	—	21 800	21 500
	—	—	—	—	21 200	
	—	—	—	—	20 000	
	—	—	—	—	20 000	
4·3	1·1	1·6	—	—	20 000	20 600
	—	—	—	—	21 800	

(Table III) is probably connected with the surface oxidation of polymer and will not be discussed here. The addition of phosphate considerably enhances the intensity of the stationary level; the presence of dibenzoyl peroxide causes a second slight increase (Fig. 4) and establishes the stationary level on the approximately same value as in the case of pure polypropylene. N-Bromosuccinimide causes a pronounced decrease in the stationary intensity of luminescence. The values of stationary intensities and initial increases in maximum are presented in Table III for various mixtures with iPP. The Table also shows the reproducibility of our measurements.

DISCUSSION

Subsequent pyrolysis of carbonized residues (obtained from iPP-NH₄Y mixture at 400°C for 10 minutes) in the presence of ammonium phosphate (1 + 3) *i.e.* under condition of a considerable dilution of the sample by the additive induces only a slight change in the concentration of paramagnetic particles (from $2.004 \cdot 10^{-2}$ to $1.445 \cdot 10^{-2}$ *a.u.*). On the other hand the presence of as little as 7.2% *wz.* of ammonium phosphate in the initial system iPP-NH₄Y decreases the ESR signal intensity from $1.615 \cdot 10^{-2}$ to $0.124 \cdot 10^{-2}$. It can, therefore, be expected that precursors of the observed paramagnetic particles in carbonized residues are formed in the condensed phase of the polymer melt. These particles react with the phosphate efficiently competing with active centres on zeolite surface. Phosphorus compounds are generally considered to be flame retardants in molten polymer phase without being active as chain-terminators in radical reactions⁴. This indicates that not only radicals are reaction intermediates here. Moreover, simple radical processes can neither account for the network consisting of aromatic cycles present in carbonized residue nor for the paramagnetism of the latter. Active centres on the available zeolite surface (centres of Brönsted and Lewis acidity²) react with hydrocarbons according to the scheme⁵:

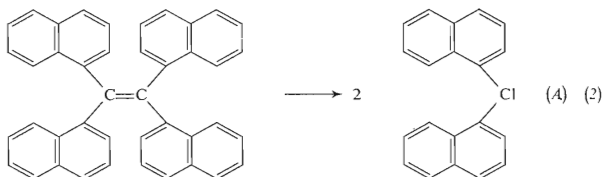


where carbonium ions give up a proton thus forming unsaturated compounds. The appearance of paramagnetism in samples of iPP pyrolysed in the presence of NH₄Y cannot be explained only on the basis of biradicals present in the conjugated system formed according to Scheme 1. The temperature dependence of signal intensity reflects only the temperature response of the ESR instrument within a broad temperature range (from ambient to liquid nitrogen temperature).

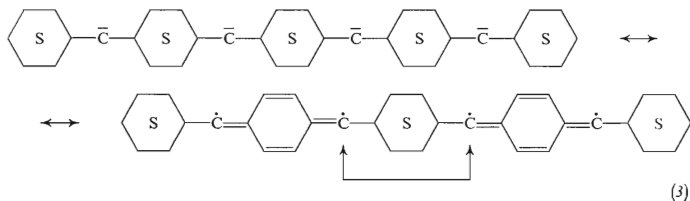
Neither the collective interaction of formed conjugated systems connected with charge transfer can be a satisfactory explanation of the observed paramagnetism of carbonized residues because these samples which could be dissolved exhibit a linear decrease of ESR signal intensity with dilution⁶. Attempts to measure the

number of oxygen molecules adsorbed on the carbonized surface revealed that a single oxygen molecule induces the disappearance of 60–70 paramagnetic centres⁷. Therefore the interpretation of the observed paramagnetism assuming the scission of single sidebonds connecting the condensed networks of aromatic cycles which gives rise to conjugated stabilized radicals is not quite satisfactory either. In order to account for the non-stoichiometric ratio in the reaction of oxygen with paramagnetic centres it is necessary to assume that the latter undergo a “polyreaction” which is initiated by oxygen molecules. This is difficult to assume in the case of simple isolated radicals or biradicals which will react with oxygen stoichiometrically.

Quite new aspects have been put forward by Franzen and Joschek⁸ who identified reaction products and found that tetra(α -naphthyl)ethylene decomposes from steric reasons already at 200°C to give 2-di(α -naphthyl)methylene according to scheme:

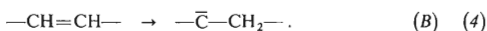


This hypothesis, which assumes the contribution of carbenes similar to A to the observed paramagnetism, offers a plausible explanation of it in carbonized samples. Carbenes can be formed through scission of double bonds connecting extensive aromatic networks. Under given experimental conditions the carbene A would react with oxygen biradical to form other biradicals which will form a network of single bonds when reacting with other available carbenes. The formation of these bonds will not be so sterically hindered as in the case of double bonds. The triplet state of monocarbene $\bar{\text{C}}$ cannot probably be observable in a semicrystalline sample by means of ESR spectrometry⁹. On the other hand the tetracarbenes exhibit a biradical character



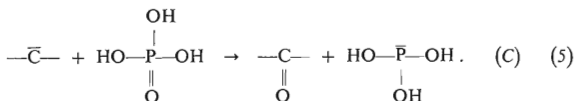
(the biradical part of molecule is denoted by an arrow while S stands for the aromatic conjugated network). If the ground state of carbene A is a triplet then these compounds should be paramagnetic even at liquid nitrogen temperatures. They would thus represent that part of paramagnetic species which disappears in an oxygen atmosphere in a non-stoichiometric way.

If scheme 1 holds then double bonds are formed on the surface of substance being degraded. It seems likely that these can be transformed to carbenes¹⁰ (type B) in an endothermic fashion, the reaction heat 192 kJ/mol being comparable with the energy of activation. The carbenes B are extremely reactive and may, together with free radicals, represent principle reaction intermediates in the process



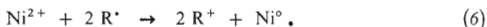
The recombination of type B carbenes leads to the formation of double bond cross-links which represent the principal skelet of the conjugated network. The latter then gives rise to paramagnetism observed in the pyrolysed sample.

A very interesting information follows also from changes of the line width. If a carbonized paramagnetic residue from iPP-NH₄Y is pyrolysed with the addition of phosphate then the line width is changed from 0.75 mT to 0.66 mT. When the original system containing iPP-NH₄Y is pyrolysed in the presence of phosphate the line width decreases as low as to 0.24 mT. Since the line width is an indirect measure of the free radical delocalization¹¹ the results indicate that in the presence of phosphate more extensive networks of conjugated systems are formed in which a relative number of side bonds is lower than that in systems pyrolysed in the absence of phosphate. This would lead to the lowering of the overall concentration of paramagnetic species. The decrease of the overall concentration of paramagnetic species which may be demonstrated by adding dibenzoyl peroxide or N-bromosuccinimide to iPP-NH₄Y system may also be induced by higher production of reactive free radicals which interact with carbenes A. In the presence of ammonium phosphate which is converted to phosphoric acid at higher temperatures the enhancement of free radical formation may be a consequence of the following reaction



Since molecule C contains a free electron pair it may form a redox system with hydroperoxides on polypropylene.

This is further corroborated by the initial increase in concentration of the Ni° formed through the reduction in the presence of small amounts of phosphate in the case of NiY zeolites (Fig. 3). It is likely that Ni° is formed via surface reaction



where R^\cdot are radicals formed from PP. The increase in concentration of the latter at given time interval of the pyrolysis results in higher level of the resulting Ni° . The decrease in concentration of Ni° at higher ammonium phosphate concentrations may be accounted for by the reaction of ferromagnetic Ni° with H_3PO_4 and by a partial regeneration if NiY zeolite.

The hypothesis about the enhancement of free radical production due to the interaction of phosphate with PP was supported by the measurement of chemiluminescence at 190°C which under these conditions reflects the rate of oxidation¹² of iPP. This, in the presence of ammonium phosphate and at 190°C , is two times higher than that of iPP alone. The concentration increase within 10–20% increases the stationary luminescence level only insignificantly. Neither two component mixtures containing phosphate–dibenzoyl peroxide and phosphate–N-bromosuccinimide or a three component system dibenzoyl peroxide–phosphate–N-bromosuccinimide (Table III) exhibit a significant influence upon the stationary luminescence level. The radical character of the observed luminescence phenomenon is clearly demonstrated by the fact that the addition of Irganox 1010 to the system reduces the luminescence intensity practically to zero and the initially self-extinguishing mixture becomes flammable.

Prooxidant effect of ammonium phosphate which may be reasonably explained by reaction (5) cannot account for the mechanism of flame retardation by phosphorus compounds. Systems containing phosphate and iPP become self-extinguishing at phosphate concentration as high as 50%; when, however, N-bromosuccinimide and dibenzoyl peroxide is present then 12–15% of phosphate is sufficient to obtain a self-extinguishing mixture.

The lack of effect on luminescence stationary level may be explained by the fact that both dibenzoyl peroxide and N-bromosuccinimide are rapidly decomposed at temperatures of luminescence measurements. The synergistic activity of these compounds may consist in their ability to react with phosphate to increase the compatibility of the latter with PP so that the efficiency is increased. Both dibenzoyl peroxide and N-bromosuccinimide might oxidize $\text{OH}-\text{P}(\text{OH})-\text{OH}$ back to some phosphoric acid derivatives which may reenter reaction (5). Selecting suitable concentrations of reaction components may lead to a system which in contact with gas burner only melts. This indicates that influencing the combustion of polymer by the synergistic action of dibenzoyl peroxide, N-bromosuccinimide and phosphate cannot be explained only by increased melt dripping, caused by extensive polymer degradation, as suggested by some authors^{13,24}.

REFERENCES

1. Blumenfeld L. A., Benderskii V. A.: Dokl. Akad. Nauk SSSR *133*, 1451 (1960).
2. Ginsburg V. L., Dain V. M.: Dokl. Akad. Nauk *131*, 785 1960.
3. Blumenfeld L. A.: Dokl. Akad. Nauk *148*, 361 1963.
4. Warren P. C.: *Stabilization Against Burning in book Polymer Stabilization*. Wiley, New York 1972.
5. Leach H. F.: Annual Reports A, London Chem. Soc. *1971*, 195.
6. Blumenfeld L. A., Voievodskii V. V., Semenov A. G.: *EPR a její použití v chemii*, p. 241. Academia, Prague 1967.
7. Tikhomirova N. N., Nikolaeva I. N., Voevodskii V. V.: *Strukt. Khim. J*, No 1, 1960.
8. Franzen V., Joschek H. J.: *Justus Liebigs Ann. Chem.* *633*, 7 1960.
9. Bersohn M., Baird J. C.: *An Introduction to Electron Paramagnetic Resonance*, p. 121. Benjamin, Amsterdam 1966.
10. Vitvickii A. I.: Dokl. Akad. Nauk *183*, 856 1968.
11. Altschuler S. A., Kozyrev B. M.: *Elektronnyi Paramagnitnii Rezonans*, p. 311. Izd. Fiz.-Khim. Lit., Moscow 1961.
12. Reich L., Stivala S. S.: *Autooxidation of Hydrocarbons and Polyolefins*. Dekker, New York 1969.
13. Hindersinn R. R.: *Polym. Conf. Ser.*, Wayne State University, Detroit, June 1966.
14. Fenimore C. P.: *Combust. Flame* *12*, 155 1968.

Translated by J. Pác.