A Study of the Interaction of Mechanically Generated Polypropylene Radicals with Phenolic Antioxidant in the Presence of Oxygen by EPR Spectroscopy

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SYNOPSIS

Isotactic polypropylene (iPP) was mechanically degraded in the absence and presence of a phenolic antioxidant at liquid nitrogen temperature in the presence of oxygen. The interaction of the primarily formed iPP macroradicals with oxygen and phenol was studied by EPR spectroscopy in the temperature region between 77 and 303 K at antioxidant concentrations of 0.1, 0.5, and 3.0 wt %. It was found that iPP macroradicals react at low temperature with oxygen, yielding peroxy radicals, and with antioxidant, with a simultaneous formation of phenoxy radicals. The development and decay of all kinds of radicals was studied. The rate constants for peroxy radical decay were determined and the apparent activation energies for the regions of slow and fast decay were calculated. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The interaction of a stabilizer molecule with a polymer is usually the main step in polymer stabilization. It represents the reaction that stops branching of degradation reactions and, in this way, shortens the kinetic chain length. The theories of thermal degradation of polymers[1-3] are based on the mechanism proposed by Bolland and co-workers.[4-7] This mechanism represents a sequence of reactions that include initiation, transfer, branching, and termination. All these reactions proceed via a radical mechanism. It is therefore clear that the EPR method can give valuable information on the reactions proceeding during polymer degradation and stabilization.

The methods of the initiation of polymer degradation represent a wide scale, among them various kinds of irradiation, heat treatment, decomposition of peroxides, and mechanical degradation. In our previous paper, we concluded[8] that the most suitable method for polymer macroradical generation is mechanical destruction. In this way, only macroradicals are formed. Formation of other radical species in the presence of additives, as in the case of the abovementioned methods, was not observed.[9]

The formation of polymer macroradicals during mechanical fracture of polymers was first observed in pioneer works by Bresler et al.[10] and Butyagin et al.[11] Later, both of them[12-16] extended their work in this field and studied processes taking place during mechanical degradation of polymers in detail: the decay of mechanically prepared macroradicals in different temperature regions; their interaction with oxygen, giving polymer peroxy radicals; and their decay. Very good reviews by Butyagin et al.,[17] Ranby and Rabek,[18] Sohma and Sakaguchi,[19] and Kausch[20] include various aspects of polymer degradation under the action of mechanical stress studies of the generation of mechanoradicals, their transformation products, and their decay.

In the previous paper,[8] we studied polypropylene macroradicals, their interaction with phenolic antioxidant, the generation of phenoxy radicals, and the decay of macroradicals and phenoxy radicals in the absence of oxygen. In this paper, we report the results obtained in the study of the same system in the presence of oxygen.

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EXPERIMENTAL

The starting polymer was an isotactic polypropylene (iPP) powder (trademark Tatren HF, Slovnaft, Czechoslovakia) that was extracted with acetone for 8 h. After drying in a vacuum oven at 303 K and 66.7 kPa for 24 h, antioxidant 2,6-di-*tert*-butyl-*p*-cresol (AO4 k, CHZJD, Bratislava, Czechoslovakia, code AP3 in Ref. 21) was impregnated into iPP powder from dichloromethane. Evaporation of the solvent by a vacuum evaporator and drying yielded iPP containing 0.1, 0.5, and 3 wt % antioxidant.

iPP powder with a different content of antioxidant was melted at 453 K and 50 MPa. A cylinder (7 mm diameter × 7 mm in length) was obtained. A hole of 2 mm diameter was drilled into the cylinder. Mechanical destruction of samples was done in a special device described elsewhere[22] at the liquid nitrogen temperature in two ways: In the first case, degradation was performed under vacuum and then oxygen was introduced at 153 K (vacuum mode). In the second case (most experiments were performed in this way), the degradation was done in the presence of air (oxygen mode).

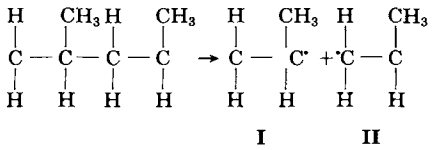
Electron paramagnetic resonance (EPR) spectra were recorded with an E-4 Varian X-band EPR spectrometer with 100 kHz modulation. The measuring cavity was annealed within a temperature of 123–303 K with an accuracy of ±1 K. The spectrometer was connected to the computer system ADAPTS. The concentration of free radicals was determined by a double-numeric integration of the EPR spectra and by a comparison with the standard STRONG PITCH fy. Varian.

RESULTS AND DISCUSSION

Analysis of Spectra

We performed mechanical degradation of iPP containing 0.1, 0.5, and 3 wt % of the commercial antioxidant of a sterically hindered phenol type (2,6-di-*tert*-butyl-*p*-cresol) in the presence of oxygen at liquid nitrogen temperature, which was compared with the degradation of pure iPP. The mechanical degradation was carried out in two different modes:

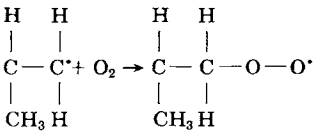
In the first case, the degradation was carried out at the liquid nitrogen temperature at high vacuum. Analysis of the spectrum of pure iPP has shown[23,24] that end macroradicals **I** and **II** are formed by a rupture of the main chain [eq. (1)] in the ratio 1 : 1:



(1)

I **II**

After introduction of oxygen at 153 K to this system, the shape of the spectrum changes drastically to an asymmetrical spectrum with a visible pattern of another component at the high-field side of the spectrum. Sohma and co-workers[19,23] demonstrated that this spectrum is a superposition of the peroxy radical **III**, which is formed in the reaction of the radical **II** with oxygen [eq. (2)], and a primary macroradical **I**:



(2)

III

In the second case, the degradation was performed at 77 K in an open system, in the presence of air. The spectrum of pure iPP obtained in this way at 123 K and heated to 273 K is demonstrated in Figure 1. The only difference between these two systems is, as will be discussed later, in the number of radicals formed. During warming to 273 K, the signal of radical **I** disappears and only a weaker signal of the peroxy radical is detected. Another conclusion that we can make is that surface radicals localized close to the surface of polymer flakes are formed during mechanical degradation. This conclusion, which is in agreement with the findings of Pilař and Ulbert[25] for mechanical degradation of poly(ethylene glycol methacrylate), follows from the fact that peroxy radicals appear in the spectra in both systems. Since the diffusion is very restricted below the glass transition temperature[26,27] and we used much lower temperatures than T_g of PP, formation of primary macroradicals **I** and **II** in the surface regions followed by a reaction with oxygen [eq. (2)] is a reasonable explanation of the processes proceeding during mechanical degradation.

Figure 2 shows the spectra obtained after mechanical degradation of iPP in the presence of oxygen at the concentration the phenolic antioxidant of 0.1 wt % taken at the temperature 123 K and then after heating to different temperatures. Quantitative considerations are given in this part. Kinetic evaluation will be presented later in this paper.

For the lowest concentration of antioxidant, which is on a technological level (Fig. 2), at the

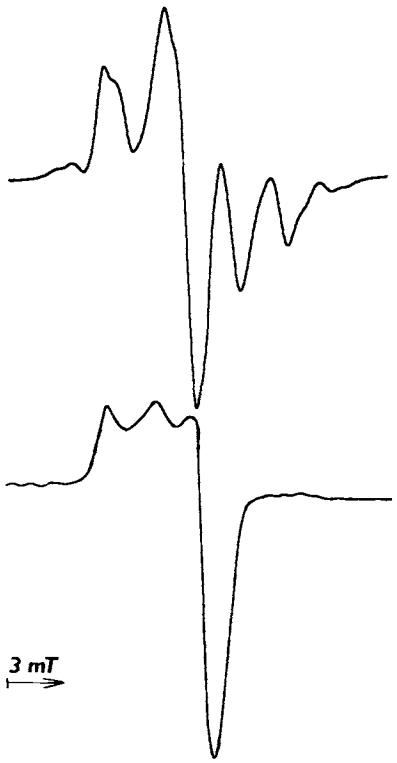


Figure 1 EPR spectrum of pure iPP destructed at 77 K in the presence of air (oxygen mode), recorded at 123 and 273 K.

lowest temperature of 123 K, the spectrum is similar to that of pure iPP. That means that it is composed of macroradical **I** and peroxy radical **III.** On raising the temperature to 153 K, another component begins to appear and patterns of macroradical **I** weaken and disappear at higher temperatures. Instead, a four-line spectrum of the phenoxy radical appears.[8,28] Phenoxy radicals are formed through abstraction of a hydrogen atom of the phenolic groups of the antioxidant by macroradical or peroxy radicals [eqs. (3) and (4)]. A further increase in temperature is followed by a decay of both kinds of radicals:

$$R^{\bullet} + InH \rightarrow RH + In^{\bullet} \quad (3)$$

$$ROO^{\bullet} + InH \rightarrow ROOH + In^{\bullet} \quad (4)$$

For the concentration of the antioxidant 0.5 wt % patterns of peroxy radicals, phenoxy radicals and a weak trace of macroradicals at the high-field side of the spectrum are visible already at 123 K. During heating, the spectrum of phenoxy radicals becomes more intense, macroradicals disappear, and signals of peroxy radicals weaken. The decay of phenoxy radicals is also observed for highest temperatures.

The strongest signal of phenoxy radicals is again observable for the highest concentration of the antioxidant of 3 wt % at 123 K together with signals of peroxy and macroradicals. The temperature effect is the same as for other antioxidant concentrations.

The stabilizing steps of the interaction of iPP macroradicals and peroxy radicals with antioxidant are reactions (3) and (4). However, reactions (2) and (3) are competitive because in both cases macroradicals are consumed. Based on our results (Fig. 2), the first view shows that the rate of the reaction of primary macroradicals with oxygen [eq. (2)] is higher than that of the corresponding reaction with antioxidant [eq. (3)]; the concentration of peroxy radicals is higher than the concentration of phenoxy radicals. However, if we consider these two bimolecular reactions from the point of view of accessibility of the reaction components, we cannot deter-

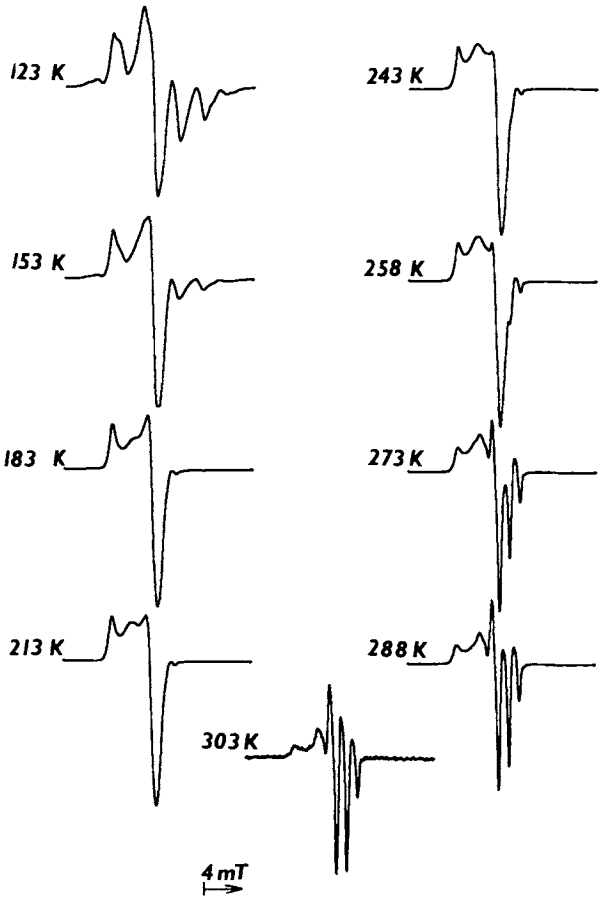


Figure 2 EPR spectrum of iPP + 0.1 wt % AO4 destructed at 77 K in the oxygen mode, recorded at different temperatures.

Table I The Time Dependence of the Concentration of iPP Macroradicals *R* Generated in the Oxygen Mode at 77 K in the Presence of Antioxidant at 123 and 153 K

	$R \times 10^{17}$ (spin/g)			
	T (123 K)		*T* (153 K)	
AO4 (wt %)	0 min	20 min	0 min	20 min
0.1	11.0	11.1	2.2	0.05
0.5	3.0	2.5	1.0	0.05
3.0	0.6	0.5	0.3	0.05

mine the ratio of the rate constants of these reactions because of the heterogeneous character of the processes as well as because of different concentrations of the reacting components. Formation of surface radicals discussed earlier during mechanical degradation makes this problem more complicated.

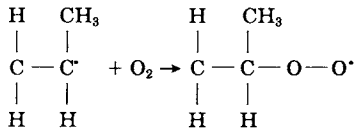
KINETICS OF RADICAL FORMATION AND DECAY

As follows from the previous part in our experimental system, the following radicals are formed and detected: primary macroradicals of iPP, peroxy radicals, and phenoxy radicals. Their presence and abundance depend on the composition of the reaction system and on the temperature. As is generally known, radicals are not very stable species and they decay or are transformed into more stable products.

Macroradicals

Macroradicals **I** and **II** are primarily formed during mechanical degradation of iPP. In the presence of oxygen, at temperatures below 120 K, radicals **II** form peroxy radicals whereas radicals **I** are relatively stable.[17,19,23] In our system, in the oxygen mode, their concentration was as high as 11×10^{17} spin/g at 123 K in the presence of 0.1 wt % AO4 (Table I) and they were stable for at least 20 min. The increase of temperature to 153 K causes a sudden drop in concentration to 2.2×10^{17} spin/g, and macroradicals decay during next 20 min to the lowest detectable level. Similar is the development of macroradicals in the presence of 0.5 and 3 wt % of antioxidant.

In the previous paper,[8] we observed that iPP macroradicals are in the absence of oxygen stable up to the α-relaxation regions of the nonstabilized as well as stabilized polymer, which is in contradiction with the present results. Both systems differ only by the presence of oxygen in the system. Then, it should follow that the interaction of macroradicals with oxygen under the formation of peroxy radicals should be responsible for the sharp drop in the amount of macroradicals **I** [eq. (5)] in the temperature region between 123 and 153 K:



(5)

On the other hand, no increase in peroxy radical concentration appears in the same temperature region (see later). A plausible explanation of this phenomenon has been suggested by Ingold and Thomas,[29,30] who assumed the formation of nonparamagnetic tetroxide from peroxy radicals via fast mutual exothermal reaction at low temperatures. The concentration effect of the antioxidant shows that the reaction of macroradicals with antioxidant must also proceed [eq. (3)]. Our previous results suggest,[8] however, that the course of this reaction is conditioned by thermal fluctuations during polymer drilling.

Peroxy Radicals

Figure 3 shows the decay of peroxy radicals of pure iPP generated under two different modes. In the oxygen mode, the initial concentration of peroxy radicals is about four times higher than in the case of the degradation in the vacuum mode. When we consider that in the absence of oxygen macroradicals **I** and **II** are generated at the ratio 1 : 1[23,24] and macroradicals **II** form peroxy radicals already at the liquid nitrogen temperature[19,23] in the oxygen mode, then the amount of peroxy radicals in the oxygen mode is eight times higher than it is in the vacuum mode. It again provides evidence that the concentration of primary macroradicals is much higher than detected. After their formation, primary macroradicals decay in a cage by recombination or they are present in the system and decay with the increase of temperature or react to more stable radicals in the presence of oxygen. In the absence of oxygen and in the presence of an antioxidant, phenoxy radicals are formed as a more stable product. In such a case, the total concentration of phenoxy and macroradicals is about 10 times higher than the concentration of macroradicals.[8] This means that about 90% of primary macroradicals decay in a cage.

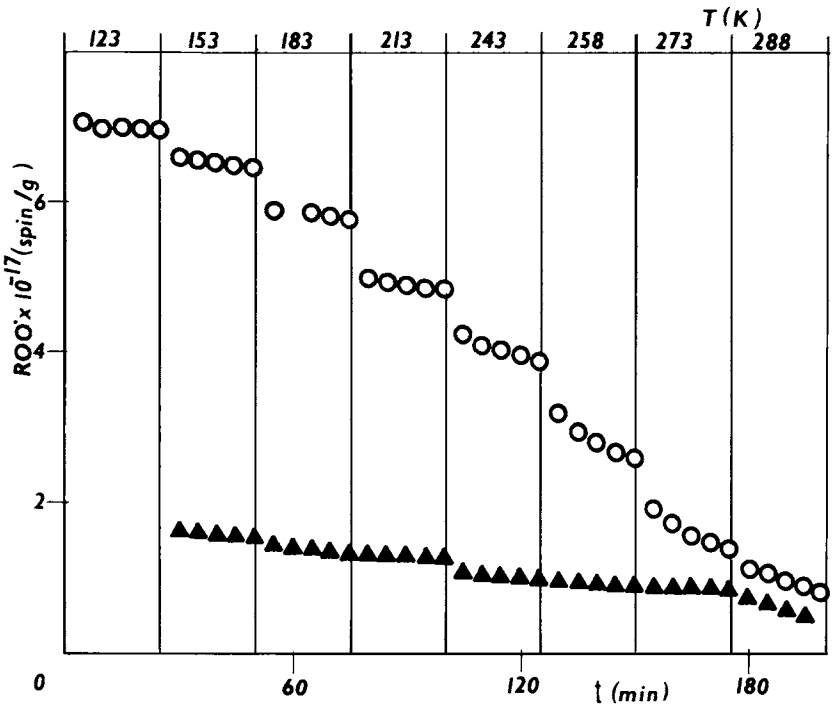


Figure 3 The temperature–time dependence of peroxy radical concentration ROO· (spin/g) for pure iPP destructed at 77 K (○) in the oxygen mode and (△) in the vacuum mode.

Another interesting phenomenon was observed under our experimental conditions. Sohma and coworkers observed that decay curves of radicals, i.e., the dependence of the radical concentration on temperature, do not show monotonous character but the concentration of radicals increases between ca. 100 K and ca. 200 K.[9,19,31,32] This process has been attributed to the formation of electric charges due to the triboelectricity and to the consecutive reactions associated with the formation of radicals in the given temperature ranges. Experimental evidence has shown that such anomalous decay was observed only for mechanoradicals generated in the presence of oxygen. No anomalous decay has been observed for the radicals produced under vacuum by γ- or UV-irradiation.[19,31] Our results show, however (Fig. 3), no increase in the concentration of radicals after heat treatment. We can thus assume that our experimental arrangement does not produce post-formation of radicals. Hence, the generation of radicals after heat treatment in the presence of oxygen is not a general phenomenon.

The heat treatment leads in both cases to the decrease in the concentration of radicals. From the mechanistic point of view, recombination of radicals giving nonradical products is most probable.[33]

Figure 4 shows the decay curve of peroxy radicals of iPP in the presence of a phenolic antioxidant. A general trend is obvious. The highest concentration of peroxy radicals is generated at the lowest concentration of the antioxidant and vice versa. This is the consequence of the competitive reactions (2) and (3). After their formation, a nearly stationary level of peroxy radicals holds up to 183 K. Then, they decay via a bimolecular reaction. It is obvious that in the presence of antioxidant the decay of peroxy radicals is faster. Although in the absence of the antioxidant there is still some level of peroxy radicals at 288 K (Fig. 3), in the presence of the antioxidant, their concentration is negligible at 273 K (Fig. 4).

We calculated the rate constants for peroxyradical decay within the temperature range from 123 to 288 K. The Arrhenius plot of this dependence is presented in Figure 5. Again, as has been shown for degradation of iPP in the absence of oxygen,[8] the Arrhenius plot shows two regions of the decay of peroxy radicals. The calculated apparent activation energies for low-temperature and for higher-temperature regions and temperatures of breaks in the Arrhenius plots are listed in Table II. The activation energies for the low-temperature region are between 0.5 and 2.0 kJ/mol. The breaks in the Arrhenius dependencies, T_b, are scattered around 230 K, which is below T_b for the decay of iPP macroradicals under vacuum.[8]

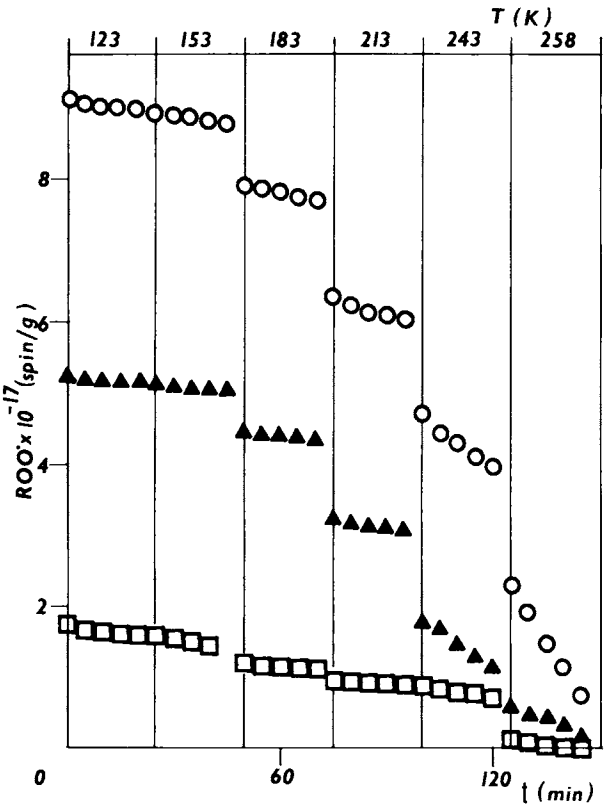


Figure 4 The temperature–time dependence of peroxy radical concentration ROO· (spin/g) for additived iPP destructed at 77 K in the oxygen mode: (○) 0.1; (▲) 0.5; (□) 3.0 wt % AO4.

On increase of temperature over 230 K, fast decay of peroxy radicals begins. The corresponding activation energies for iPP with additives are higher than those for nonstabilized polymer. That means that the reaction of peroxyradicals with the antioxidant (eq. 4) is more temperature-dependent than is the decay of peroxy radicals. The activation energy values vary between 88.8 kJ/mol for the antioxidant concentration 0.1 wt % and 103.6 kJ/mol for the sample with 3.0 wt % of antioxidant.

The decay of peroxy radicals proceeds via recombination[34a] and/or in the presence of an antioxidant by reaction with antioxidant molecules. A question arises whether these reactions proceed in a kinetic regime or whether they are diffusion-controlled. This question has not been fully answered.[34b] The breaks in Arrhenius plots (Fig. 5) and the flat profile of the peroxy radical decay at low temperatures (Fig. 4) show that heat is necessary to ensure some significant rate of peroxy radical reactions. Abrupt changes of activation energies show, rather, that diffusion processes are decisive.

Phenoxy Radicals

Figure 6 shows the development of phenoxy radicals generated in the oxygen mode. It is evident that the development of phenoxy radicals differs from that of iPP macroradicals and peroxy radicals (Fig. 4). For all concentrations of antioxidant, the development of phenoxy radicals is not monotonous but passes through a maximum. For lower concentrations of antioxidant, after a rather flat development at low temperatures, phenoxy radical concentration starts to increase at 213 K and passes through a maximum between 243 and 258 K. Then, the decay of phenoxyradicals starts. For a high concentration of the antioxidant (3 wt %), the amount of phenoxy radicals increases already at 123 K. The maximum is again at about 243 K and then the decay begins. For the decay of phenoxy radicals, bimolecular disproportionation well discussed by Pospíšil[35] has been suggested.

The increase of phenoxy radical concentration is evidently the consequence of their stabilization step, e.g., the reactions with peroxyradicals (eq. 4). However, the development of phenoxy radicals (Fig. 6) does not follow the decay of peroxy radicals (Fig. 4). At low antioxidant concentrations (0.1 and 0.5 wt %), the decay of peroxy radicals in the temperature range between 123 and 243 K is faster than is the development of phenoxy radicals, and at higher temperatures, the increase of phenoxy radicals is smaller than is the decrease of peroxy radical concentration. For high antioxidant concentration (3 wt %), on the other hand, the instantaneous increase of the amount of phenoxy radicals at 123 K and further growth up to 243 K does not correspond to the flat profile of peroxy radical decay. We must therefore conclude that the reaction of peroxy radicals with antioxidant molecules (eq. 4) is not the sole reaction of peroxy radical decay. A reasonable

Table II Apparent Activation Energies of Peroxy Radical Decay for Low-temperature Region (E_{Al}), for Higher-Temperature Region (E_{Ah}), and Temperatures of the Break (T_b) of the Arrhenius Dependence for Pure and Additived iPP Destructed in the Oxygen Mode

Sample	E_{Al} (kJ/mol)	E_{Ah} (kJ/mol)	T_b (kJ/mol)
Pure iPP	0.5	39.5	230
0.1 wt % AO4	2.0	88.8	232
0.5 wt % AO4	1.6	98.7	227
3.0 wt % AO4	1.6	103.6	234

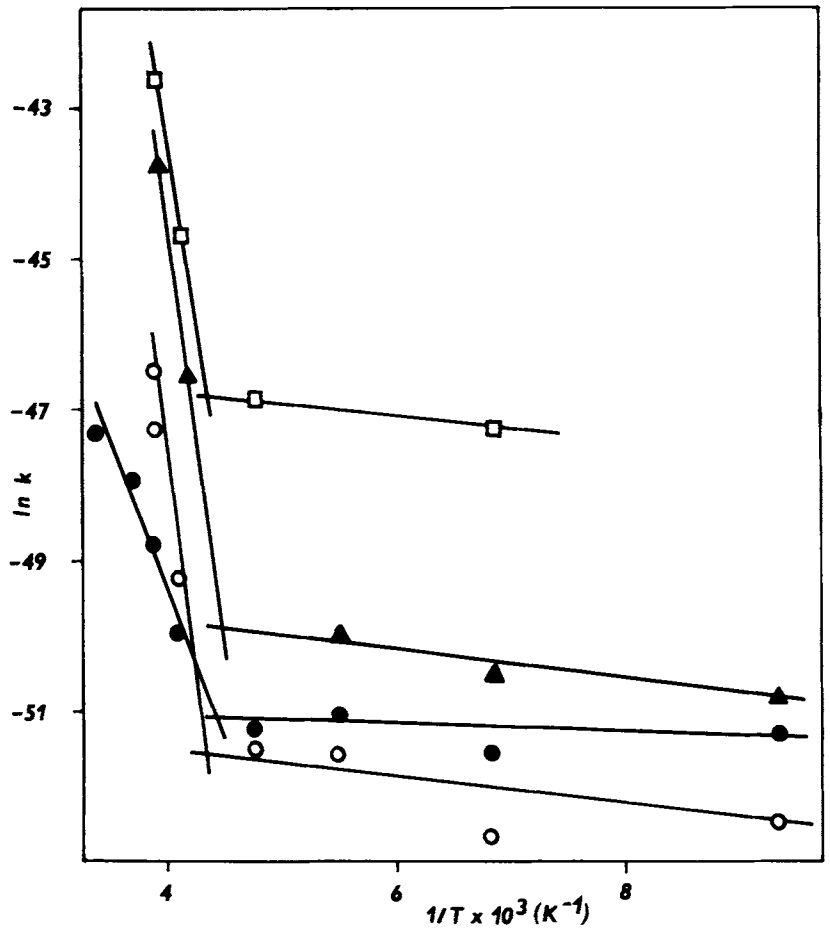


Figure 5 The Arrhenius plot of the decay of peroxy radicals: (●) pure iPP; (○) 0.1; (▲) 0.5; (□) 3.0 wt % AO4.

explanation of this phenomenon is the recombination of peroxy radicals[34a] with the formation of nonradical products.

To analyze changes in the phenoxy radical concentration, we must consider all possible reactions of the formation of phenoxy radicals. They include

(a) reaction of iPP macroradicals with antioxidant (eq. 3), and

(b) reaction of peroxy radicals with antioxidant (eq. 4).

However, the sum of both kinds of radicals for the system with 3 wt % of antioxidant, 0.6×10^{17} spin/g iPP macroradicals (Table I) and 1.75×10^{17} spin/g peroxy radicals (Fig. 4), is much lower than is the maximum amount of phenoxy radicals: 13.2×10^{17} spin/g. The reasonable explanation is as follows: As mentioned earlier, Ingold and Thomas[29,30] assumed formation of nonparamagnetic tetroxide by recombination of peroxy radicals at low temperature. Pilař and Ulbert[25] expected formation of polymeric tetroxide from about 75% of primarily generated macroradicals in the case of poly(ethylene glycol methacrylate). Tetroxides are unstable compounds and Bartlett and Guaraldi[36] observed that the equilibrium reaction is completely reversible within the temperature range between 123 and 203 K in the absence of any radical scavenger. With temperature increase, tetroxides decompose, giving rise to oxygen, alkoxy radicals, and further products.[29,30] Alkoxy radicals can yield peroxides and the complete sequence of these reactions is given in eq. (6):

$$2\ \mathrm{ROO^{\cdot}} \rightleftarrows \mathrm{ROO-OOR} \rightarrow \mathrm{RO^{\cdot}} + \mathrm{O_2} + {}^{\cdot}\mathrm{OR} \rightarrow \mathrm{ROOR} + \mathrm{O_2} \quad (6)$$

In the presence of an antioxidant, we can assume a rapid interaction of alkoxy radicals with antioxidant molecules [eq. (7)]:

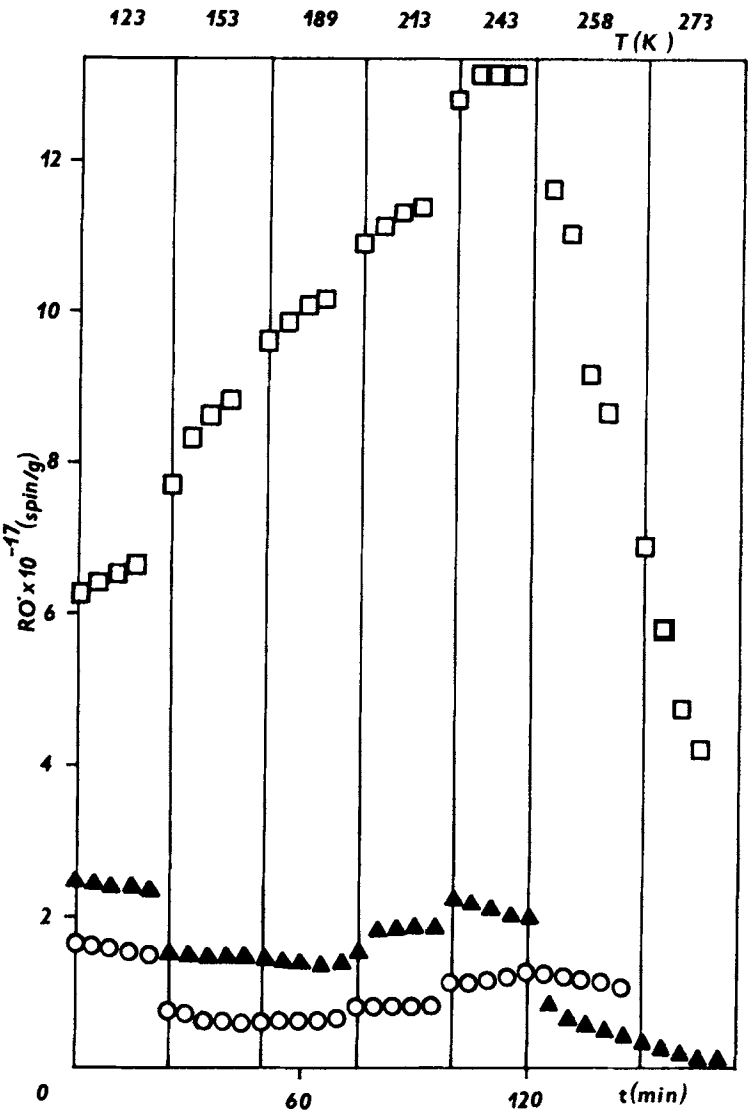


Figure 6 The temperature–time dependence of phenoxy radical concentration RO$^{\bullet}$ (spin/g) for additived iPP destructed at 77 K in the oxygen mode: (○) 0.1; (▲) 0.5; (□) 3.0 wt % AO4.

$$RO^{\bullet} + InH \rightarrow ROH + In^{\bullet} \quad (7)$$

which yields a more stable phenoxy radical and a hydroxy group. This reaction causes exhaustion of tetroxide at the increase in temperature and twofold increase in phenoxy radical concentration.

It is obvious that the molecule of a radical scavenger must be in the vicinity of the decaying tetroxide. That is probably the reason why we do not observe this effect at low antioxidant concentrations. Since at temperatures below T_g of the polymer diffusion is very restricted,[26,27] at low antioxidant concentration, this effect is seen only at temperatures close to T_g when the mobility of chain segments releases, allowing, thus, diffusion of antioxidant molecules to the neighborhood of peroxy and alkoxy radicals. However, at those temperatures, the concentration of peroxy radicals falls down and the increase in radical concentration is small.

For the degradation in the absence of oxygen,[8] the increase in the phenoxy radical concentration was shown not to be a pure process but it was overlapped by a simultaneous decay of these radicals. The calculation of the rate constants for phenoxy

radical growth and/or decay without separation of individual processes would not, therefore, make any physical sense.

CONCLUSION

During mechanical degradation of iPP in the presence of oxygen at the liquid nitrogen temperature in addition to sterically more hindered iPP macroradicals, peroxy radicals are formed. In the presence of a phenolic antioxidant also, phenoxy radicals are generated. The ratio of particular radicals depends on the concentration of antioxidant in the system. The increase in temperature causes decay of radicals. The fast decay of macroradicals starts at 153 K. The decay of peroxy radicals proceeds very slowly below 240 K. At over 240 K, the fast decay of peroxy radicals occurs. Development of phenoxy radicals is concentration-dependent and passes through a maximum at about 240 K. The interpretation of the development and decay of peroxy radicals and phenoxy radicals includes the formation of polymeric tetroxides and their subsequent decomposition.

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