

A Study of the Interaction of Mechanically Generated Polypropylene Radicals with Phenolic Antioxidant in the Absence of Oxygen Using ESR Spectroscopy

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Synopsis

Polypropylene (PP) was mechanically degraded in the absence and in the presence of a phenolic antioxidant, 2,6-di-*t*-butyl-*p*-cresol. The interaction of macroradicals of PP with the antioxidant was studied by ESR spectroscopy in the temperature region between 77 and 303 K and at antioxidant concentrations of 0.1, 0.5, and 1.5 wt % in the absence of oxygen. In the absence of the antioxidant, the end macroradicals of PP are formed which decay with increase in temperature. In the presence of antioxidant both macroradicals of PP and phenoxy radicals are generated. The PP macroradicals are very stable up to the temperature close to T_g of the polymer. Beyond this temperature they decay via bimolecular mechanism—according to the second-order kinetics. The rate constants for PP macroradicals decay were determined, and the apparent activation energies for the regions of slow and fast decay were calculated.

INTRODUCTION

Polyolefins belong to polymers very sensitive to various types of physical degradation. By subjecting polyolefins to heat, various kinds of radiations, and mechanical stress main chain scission takes place; consequently, their mechanical properties worsen. These degradation processes are considerably accelerated in the presence of oxygen.^{1,2}

Degradation processes of polyolefins are influenced on adding various kinds of stabilizers which should lower the rate of degradation via reactions with various radicals formed by main-chain scission, isomerization, and free-radical transfer.

We used ESR spectroscopy for studying interaction and decay of free radicals of polypropylene generated by mechanical destruction of polypropylene at liquid nitrogen temperature in the absence of oxygen with sterically hindered phenol as a thermooxidation stabilizer. Formation and decay of phenoxy radicals in the temperature interval between 77 and 303 K were examined.

EXPERIMENTAL

Commercial powder isotactic polypropylene (iPP), Tatren HF (Slovnaft Bratislava, Czechoslovakia) was extracted with acetone for 8 h. After drying in a vacuum over at 303 K and 66.7 Pa for 24 h, antioxidant 2,6-di-*tert*-butyl-

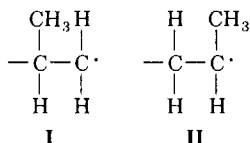
p-cresol (A04 k-CHZJD Bratislava, Czechoslovakia—code AP3 in ref. 3) was impregnated into polypropylene powder from dichloromethane. After evaporating the solvent on a rotary vacuum evaporator and drying, the samples of pure isotactic polypropylene and the samples containing 0.1, 0.5, and 1.5 wt % of stabilizer were prepared in press-temperature equipment⁴ at 453 K and 50 MPa. A cylinder (7 mm diameter \times 7 mm length) was obtained. A hole of 2-mm diameter was drilled into the cylinder. Evacuation of cuvettes and mechanical destruction of samples was done in specially prepared glass ampules under vacuum 5×10^{-5} mm Hg with a vidium (special) drill (4-mm diameter). The ampules were dipped into liquid nitrogen during destruction.⁵

Free radicals were measured on an E-4 Varian X-band ESR spectrometer with 100 kHz modulation. The spectrometer was connected to the computer system ADAPTS. The concentration of free radicals was determined by a double-numeric integration of the ESR spectra and by comparison with the standard Strong Pitch, fy. Varian.

RESULTS AND DISCUSSION

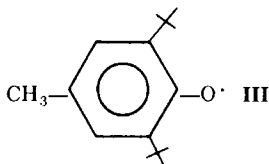
Preliminary experiments showed that the most suitable mode of macroradical generation in the study of the interaction of phenolic antioxidants with polypropylene is mechanical destruction. In this way only macroradicals are formed. The generation of macroradicals by γ -radiation or by peroxide decomposition yield other types of radicals as a result of interactions between radiation and antioxidant.

Figure 1 shows the ESR spectrum of the mechanically destructed pure iPP measured at 77 K and after heating to 303 K. The spectrum obtained corresponds to radicals I and II^{6,7}:



The shape of the spectrum does not vary over the wide temperature range.

Figure 2 shows the ESR spectrum of the destructed sample of iPP containing 0.5 wt % of antioxidant A04 at 77 K in the absence of oxygen. Under the same conditions of destruction and measurement, another one component is observed in the spectrum. After heating the sample to 303 K, we observed residual macroradicals of iPP in side lines of the spectrum and a distinct four-line spectrum with the line width of ca. 0.8 mT in the center (Fig. 3). The spectrum of the phenoxy radical III has been described elsewhere⁸ and is



characterized by hyperfine splitting constants $a_{\text{H}_{3,5}} = 0.14$, $a_{\text{H}_{2,6}}^{\text{CH}_3} = 0.6$, $a_{\text{H}_4}^{\text{CH}_3} = 1.195$ mT. After simulation using the above constants and the line width of 0.8 mT, we obtained the spectrum in Figure 4, which is almost

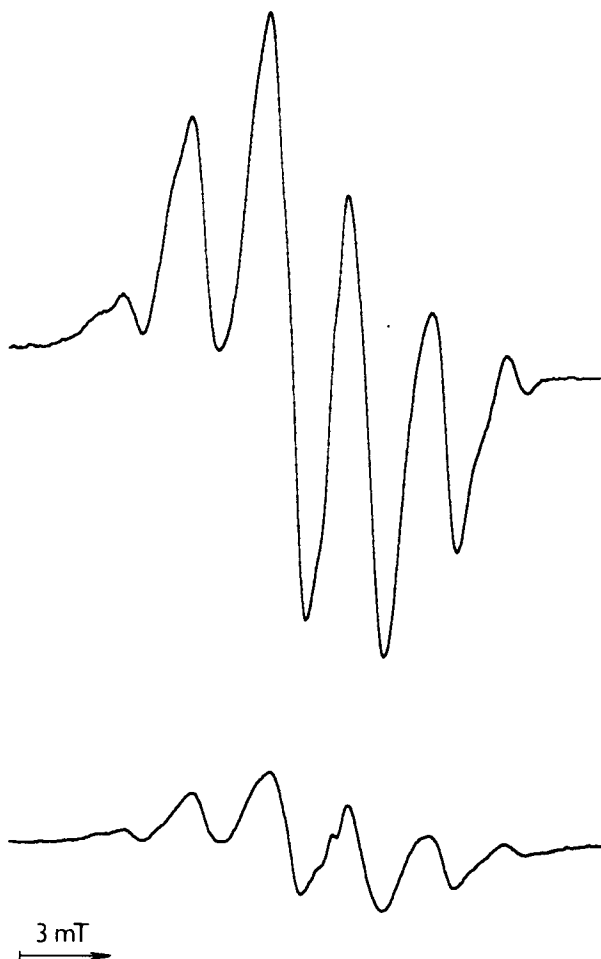


Fig. 1. ESR spectrum of destroyed pure iPP measured at (A) 77 K; (B) 303 K.

identical with the spectrum in Figure 3. This indicates that phenoxy radicals are generated during mechanical destruction of iPP in the presence of antioxidant.

Sohma and co-workers⁹ found that no radicals are formed in the mechanical destruction of the low-molecular weight organic compounds. Radicals are only produced from the mechanically fractured solid macromolecules. It is then reasonable to assume that the formation of phenoxy radical III is brought about by an interaction of macroradicals I and II with the antioxidant molecules. This reaction is analogous to the reaction of macroradicals of polybutadiene (P^{\cdot}) with inhibitor (InH), observed by Sohma^{10,11}:



It is difficult to assume that the main chain scission during mechanical destruction takes place in the vicinity of additive molecules. Their concentration in our experiments (0.1–1.5 wt %) is much lower than the number of

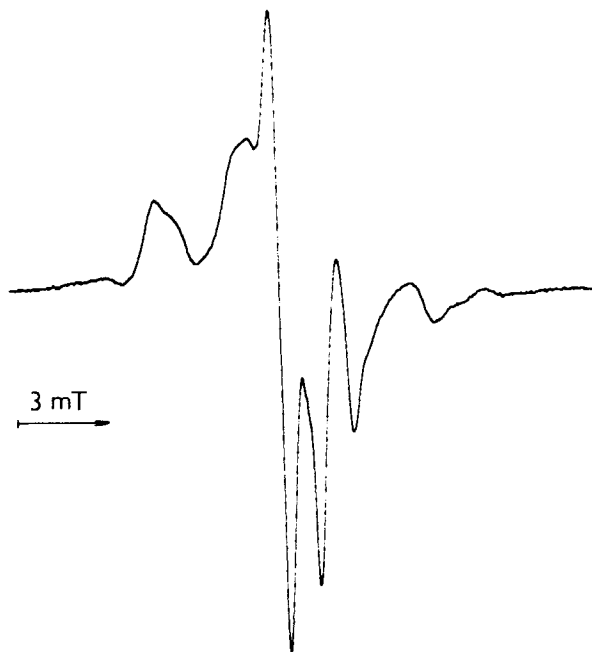


Fig. 2. ESR spectrum of mechanically degraded iPP sample +0.5 wt % of the stabilizer A04 measured at 123 K.

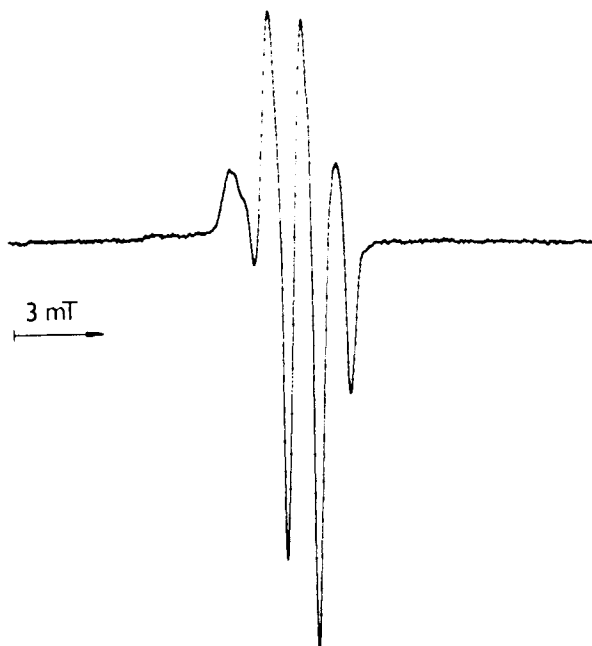


Fig. 3. ESR spectrum of destructed sample of iPP a 0.5 wt % of the stabilizer A04 measured at 303 K.

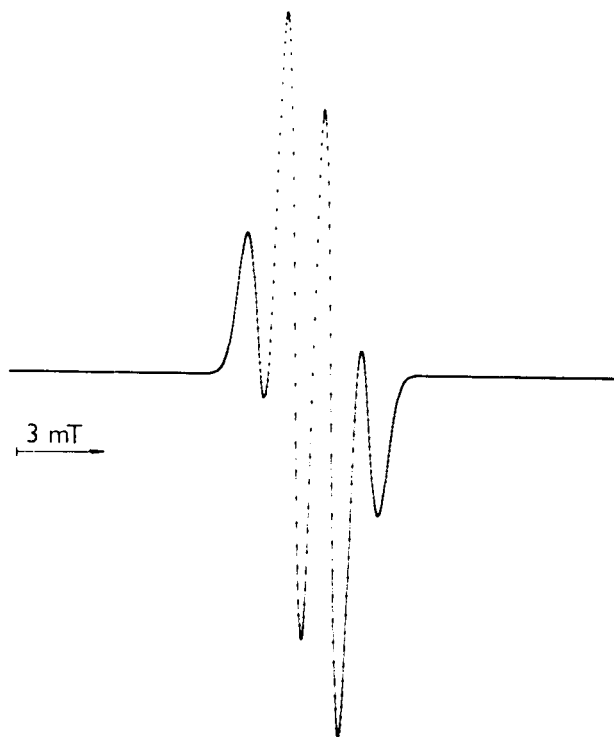


Fig. 4. ESR spectrum simulated on an ADAPTS computer—phenoxy radical.

C—C bonds in the polymer. Diffusion of larger organic molecules is assumed to be retarded¹² at temperatures below T_g of the polymer in the frozen state. Bimolecular reaction of the formation of the radical of antioxidant [eq. (1)] is possible owing to local temperature fluctuations during mechanical destruction. In this process, the segmental motions of macromolecules and of antioxidant are released since decay curves of phenoxy radicals (Fig. 5) display remarkable concentration stability up to the relaxation region of the polymer matrix.

KINETICS OF RADICAL DECAY IN THE SYSTEM iPP-ANTIOXIDANT

The kinetics of the radical decay was studied over the temperature interval between 77 and 303 K for the samples of pure iPP and iPP containing 0.1, 0.5, and 1.5 wt % of antioxidant. We examined the decay of macroradicals I and II of pure and stabilized iPP as well as the kinetics of the formation and decay of radicals of antioxidant III. The amount of individual radicals was determined by an analysis of mixed spectra using the ADAPTS computer.

Pure iPP was mechanically degraded at 77 K and radicals I and II were formed. Figure 5 (curve 1) shows the decay of these radicals. Almost no radical decay was observed up to 258 K. Rapid decrease of the radical concentration starts from 273 K. From the mechanistic point of view, recombination of macroradicals under formation of nonradical products is most probable.¹⁰

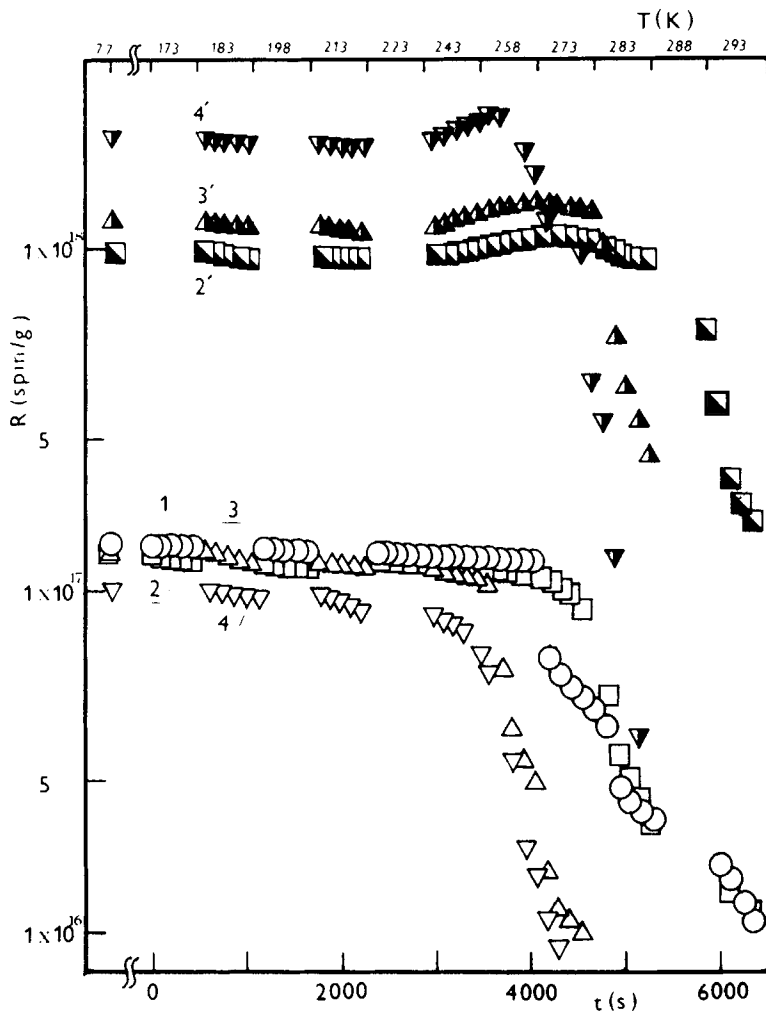


Fig. 5. The time and temperature dependence of the concentration of macroradicals of iPP and phenoxy radicals in pure iPP (curve 1, \circ), and in the presence of 0.1 (curves 2, and 2', \square and \blacksquare), 0.5 (curves 3, and 3', \triangle and \blacktriangle), and 1.5 wt % (curves 4, and 4', ∇ and \blacktriangledown). Open symbols correspond to macroradicals and half-open symbols to phenoxy radicals.

In the presence of antioxidant, iPP macroradicals and phenoxy radical were detected. The latter was generated during mechanical destruction of stabilized iPP. Decay curves for both types of radicals are shown in Figure 5, where the curves 2, 3, and 4 describe the decay of iPP macroradicals and 2', 3', and 4' show the behavior of phenoxy radicals at the antioxidant concentration of 0.1, 0.5, and 1.5 wt %, respectively. The overall population of radicals is evidently much higher in the presence of antioxidants than in pure iPP.

Much higher concentration of free radicals must be formed during mechanical destruction of pure iPP than is observable after destruction. If the system contains 1.5 wt % A04, the overall concentration of free radicals (macroradicals and phenoxy radicals) is 1 order of magnitude higher than the concentra-

tion of free radicals in iPP without A04. We can conclude (Fig. 5) that over 90% of generated macroradicals decays during destruction. A considerable portion of primary macroradicals is trapped by radical scavengers in the presence of antioxidants. The number of main chain scissions is at least by 1 order of magnitude greater than the number of free radicals observed in the mechanically destructed polymer without radical scavenger.

It is characteristic of decay curves of macroradicals in the presence of antioxidant that the decay begins at lower temperatures than that of pure iPP. At the antioxidant concentration of 0.1 wt %, macroradical concentration starts to gradually decrease at 245 K. At antioxidant concentrations of 0.5 and 1.5 wt %, the decay occurs at 243 and 238 K, respectively. The decay rate is higher for higher concentrations of an additive. The reduction of the initial temperature of macroradical decay by 25 K can be explained in two ways:

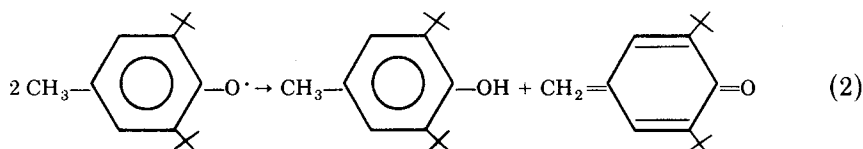
1. By a release of segmental mobility of macroradicals as a result of the temperature rise of the sample below T_g so that the transport of the molecules of additive to the vicinity of polymer macroradicals is possible (α -relaxation effect).

2. By a plastification effect of additive, which would lead to the lowering of T_g and again to the release of segmental motion of macromolecules.

Both mechanisms lead to the concentration increase of phenoxy radicals occurring in the same temperature region as the initial decrease in macroradical concentration (curves 2', 3', and 4' in Fig. 5). This indicates that no interaction between macroradicals and antioxidant occurs in the frozen state. This reaction takes place after the release of the segmental motion of macroradicals. This fact supports the theory that diffusion processes of antioxidant will be decisive.

We can assume from an increase in the concentration of phenoxy radicals (curves 3' and 4', Fig. 5) that generation of radicals by mechanical destruction does not lead under the given conditions to complete consumption of antioxidant from the system. Part of antioxidant remains in the molecular form and reacts with macroradicals in the α -relaxation region. However, in every case, whether in the generation of radicals or on subjecting polymer to heat, reaction (1) takes place, which is the stabilization step. If the concentration of phenoxy radical starts to increase and macroradicals of iPP begin to decay at the same temperature, one can expect that the increase in the concentration of antioxidant radicals will not be a pure process but will be overlapped by a simultaneous decay of this radical. The part of the decay curve illustrating the concentration increase of phenoxy radical is thus a superposition of the growth and decay curves.

A rapid decrease of the concentration of phenoxy radical occurs at the concentration of 1.5 wt % of antioxidant at 243 K, 0.5 wt % at 273 K, and 0.1 wt % at 283 K (curves 2', 3', and 4', Fig. 5). Phenoxy radicals may decay through bimolecular disproportionation,^{13,14} which gives the original molecule of antioxidant and quinone methide:



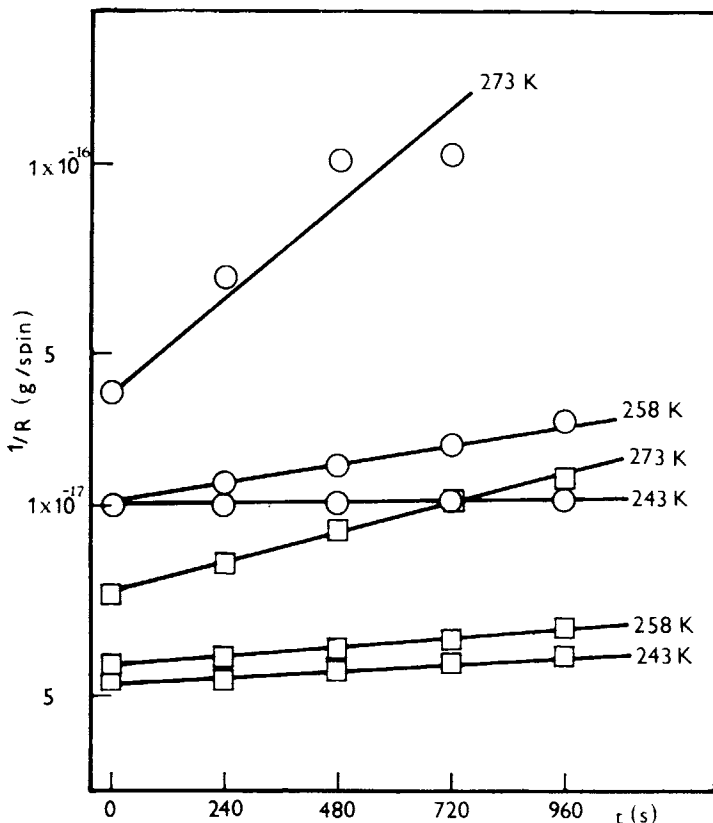


Fig. 6. The time dependence of the reciprocal of iPP macroradicals concentration in the presence of 0.1 wt % (\square) and 1.5 mass % (\circ) A04 at different temperatures.

The time dependence of the reciprocal of macroradical concentration for the concentration of antioxidant 0.1 and 1.5 wt % is illustrated in Figure 6 for temperatures 243, 258, and 273 K. The dependences are linear, and we assume that it is a second-order reaction. We used the computer analysis of the ESR spectra for calculating the rate constants for bimolecular reaction at various temperatures.

Figure 7 shows the Arrhenius dependence of the decay of macroradicals of pure and additive iPP. The relationship shows two regions of macroradical decay. Apparent activation energies for the decay of iPP macroradicals calculated in the low-temperature region E_{Al} and in the range of higher temperatures E_{Ah} , and the temperature of the break on the Arrhenius dependence T_b are listed in Table I.

Figure 7 and Table I show that the macroradical decay is almost negligible with very low activation energy in the low-temperature region; we have the corresponding values for the apparent activation energy from 0.24 kJ/mol for pure iPP to 1.94 kJ/mol for a polymer containing antioxidant (1.5 wt %). Apparent activation energies are higher within the higher temperature region: between 60.25 kJ/mol for iPP containing 0.1 wt % of inhibitor and 94.1 kJ/mol for a polymer with 1.5 wt % of antioxidant.

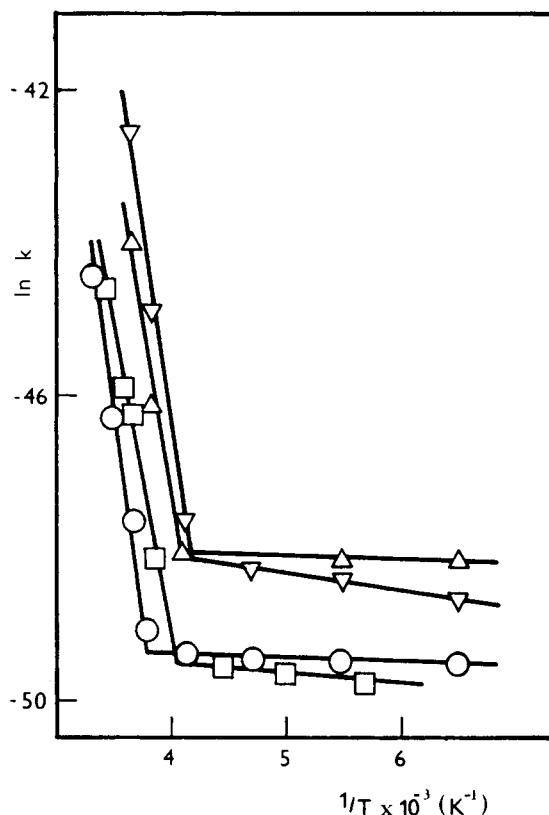


Fig. 7. Arrhenius plot of the decay of iPP macroradicals: (○) pure iPP; (□) 0.1 wt % A04; (Δ) 0.5 wt % A04; (▽) 1.5 wt % A04.

The temperature T_b for pure iPP is 263 K, which is in very good agreement with the average value of T_g reported.¹⁵ The temperature T_b is shifted to lower temperature region in the presence of antioxidant; for the concentration of the additive of 1.5 wt % it is shifted by as much as 25 K. If for pure iPP the break on the Arrhenius dependence corresponds to T_g of the polymer, it is also reasonable to assume that in the presence of antioxidant the respective break will correspond to T_g of the additived polymer. This increases in T_b is, as has already been discussed, probably caused by the plastification effect of additive.

TABLE I
Apparent Activation Energies for Low-Temperature Region E_{Al} , for Higher Temperature Region E_{Ah} , and Temperatures of the Break on the Arrhenius Curve for Pure and Additive iPP

| Sample | E_{Al} (kJ/mol) ^a | E_{Ah} (kJ/mol) ^a | T_b (K) |
|--------------|--------------------------------|--------------------------------|-----------|
| Pure iPP | 0.24 (0.99) | 65.79 (0.99) | 263 |
| 0.1 wt % A04 | 0.81 (0.99) | 60.25 (0.98) | 245 |
| 0.5 wt % A04 | 0.61 (0.90) | 72.66 (0.99) | 243 |
| 1.5 wt % A04 | 1.94 (0.99) | 94.08 (0.99) | 238 |

^aValues in parentheses = the size of correlation coefficient.

CONCLUSIONS

In this research we studied the mechanical degradation of isotactic polypropylene (iPP) in the presence or in the absence of a sterically hindered phenol type antioxidant by means of ESR spectroscopy in the absence of oxygen. For pure iPP the presence of macroradicals was observed, while, in the presence of the antioxidant, polymer radicals and phenoxy radicals were detected. Phenoxy radicals are formed through the interaction between iPP macroradicals and the antioxidant as a result of temperature fluctuations during the polymer degradation. The total population of radicals is about 1 order higher in the presence of the antioxidant. Therefore, we conclude that, during mechanical degradation of iPP at liquid nitrogen temperature, the primary macroradicals decay in the cage.

The decay of macroradicals and phenoxy radicals was studied in the temperature region between 77 and 303 K. The iPP radicals are very stable up to the temperature close to T_g of the polymer. Beyond this temperature they decay via bimolecular mechanism. In the presence of antioxidant, the beginning of the iPP macroradicals fast decay is shifted to lower temperatures, depending on the antioxidant concentration. For the antioxidant concentration of 1.5 wt %, this shift is as much as 25 K. The rate constants of the radicals decay were determined. For both types of radicals, a two-stage decay process is characteristic. A slow process for low temperatures, and fast decay for higher temperatures. The apparent activation energies for the regions of slow and fast decay were calculated.

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