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Study of fast processes in oxidized polypropylene in the presence of pyrene

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Abstract

The study of oxidized polypropylene, undoped and doped with pyrene was carried out with the main aim of investigating energy and charge transfer in these systems. The transient absorption spectrum of trapped electrons was not detected in the case of oxidized polypropylene because of electron scavenging by products of polymer oxidation (peroxides and carbonyl groups). In doped oxidized polypropylene, transient absorption bands due to pyrene radical anions ($\lambda_{max}=500$ nm) and cations ($\lambda_{max}=450$ nm) were observed. The yields of these bands in this system were lower than in non-oxidized polypropylene. The ratio of absorption at 450 nm and 500 nm was different in these polymer matrices, too. Relatively less pyrene radical-anions were generated in oxidized system. The pulse irradiated pyrene-oxidized polypropylene system generated much weaker emission attributed to pyrene monomer fluorescence than in non-oxidized polymer. All these results suggested that oxidized polypropylene matrix interacted with primary charges hence, pyrene radical ions yield and solute ion-recombination leading to excited state formation was limited. © 1998 Elsevier Science S.A.

Keywords: Polypropylene; Oxidized polypropylene; Pyrene; Ionic processes; Pulse radiolysis; Laser excitation

1. Introduction

Polypropylene is well known for its susceptibility to oxidation forced by heat, UV or ionizing radiation [1–13]. Stabilization of polypropylene against different type of degradation agents can be achieved by controlling the radical reactions as well as the oxidation reactions. While radical processes depend on the morphology of the polypropylene, the oxidation reactions can be controlled by the incorporation of certain stabilizers. The hindered phenols and amines have been widely used as the anti-oxidants for photostabilization of polyolefines [14]. The protection mechanism of antioxidants dissolved in polypropylene γ-irradiated under common conditions has been investigated quite recently [15].

Anti-oxidants, during the irradiation of commercial polypropylene, suffer decomposition [15–20] and as a result, the protection efficiency of stabilizers ought to decrease with irradiation dose, hence, oxidation can not be stopped as much as one might expect.

This discussion leads to the conclusion that during the irradiation of commercial polypropylene in the presence of oxygen, in fact, partly oxidized polymer should be present in spite of the protective action of anti-oxidants [9,18]. In pulse irradiated oxidized polypropylene, IR transient absorption attributed to trapped electrons was not detected [21].

The present work, for the first time, involves pulse radiolysis study of ionic and excited species produced in pyrene-doped oxidized polypropylene. The main aim of this investigation concerns the protective mechanism of aromatic additives in such complex polymeric system.

2. Experimental details

The isotactic polypropylene (PP), ~50% crystallinity, was produced by Great Lakes of Milan (Italy); samples were ca. 60 μm thick film containing ca. 50 ppm irganox 1076. PP was additionally purified by soaking for several weeks using n-hexane (puriss. Fluka) with repeated changes of the solvent.

Oxidized polypropylene (o-PP) was produced by radiation-induced oxidation of PP (dose ~45 kGy) according to the method described elsewhere [9]. The concentration of carbonyl groups was determined using quantitative FTIR and by iodometry with spectrophotometric titration of the I_3^-. Using these methods, the concentration of carbonyl groups, treated as a probe of oxidation progress, was estimated to be

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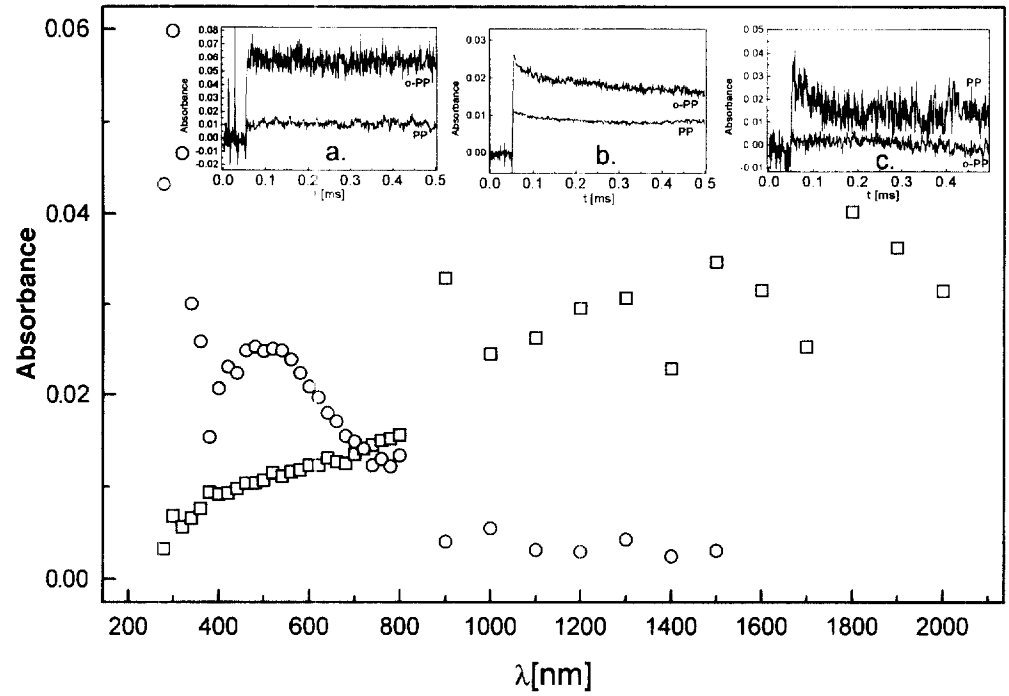

Fig. 1. Optical spectra of pulse irradiated PP (□) and o-PP (○) taken 10 μs after the 4 μs pulse at 100 K; ~0.08 cm thick sample. Insets: Absorption-time profiles for these two matrices measured at: (a) 300 nm; (b) 500 nm; (c) 1500 nm.

ca. 2×10^{-2} mol dm^{-3} after 24 h of air exposure at room temperature.

Pyrene, Py (analytical grade, UEB Belgium) after the crystalization from ethanol was additionally purified by sublimation.

Acceptor molecules were introduced into any kind of polypropylene by immersing the previously purified polymeric film in solution (*n*-hexane) containing acceptor for at least one week in order to establish an equilibrium concentration of the additive in polymer sample. Afterwards, the sample was rinsed with methanol to remove traces of acceptor from the surface. The polymer film strips were dried in vacuum (10^{-4} Torr for 20–25 h).

The Py concentration in polymer film was determined spectrophotometrically using diode array spectrophotometer Hewlett-Packard, HP 8452.

The pulse radiolysis measurements were carried out using a linear electron accelerator ELU-6 (USSR made) which delivered 17 ns (ca. 40–50 Gy), 1 μs (ca. ~250 Gy) and 4 μs (ca. ~500 Gy) pulses. The home-made styrofoam–copper cryostat enabled experiments at temperatures down to 100 K. More details concerning the detection and accelerator systems can be found elsewhere [21–23].

In time-resolved photoexperiments polymer doped samples were excited at $\lambda_{exc}=337.1$ nm by single light pulses (duration about 300 ps, energy up to 78 μJ) provided by a nitrogen laser (Laser Photonic, model LN 120C). The emission, through the monochromator (Bausch & Lomb, 1350 grooves/mm, slit setting 0.1) was detected using Hamamatsu IP 28 photomultiplier. The signal was recorded with a digitizing oscilloscope HP 54510 A and transferred via an interface to an IBM-AT computer for data storage and analysis.

3. Results and discussion

Fig. 1 shows the absorption spectra of pulse irradiated, deaerated PP and o-PP films measured at 100 K. No IR absorption responsible for trapped electrons, e_t^- was detected for o-PP matrix. The new, strong absorption bands in the visible and UV ranges were found there, which could be attributed to the intermediates generated probably as a result of e_t^- reaction with the products of PP oxidation. All these events occurred during the 4 μs pulse (Fig. 1, inserts). The time dependence of the after the pulse absorptions taken at 300 nm and 500 nm for o-PP film strongly suggested that the species responsible for these bands were different.

The absorption spectra of pulse irradiated at 273 K (1 μs pulse) PP and o-PP, both doped with Py are shown in Fig. 2. The assignment of the absorption bands centred at 450 nm and 500 nm to the Py radical-cation ($Py^{\bullet+}$) and -anion ($Py^{\bullet-}$) respectively is consistent with the spectra reported previously [21,24]. The yields of these species were lower in o-PP matrix as compared with PP system. The ratio of absorption at 450 nm and 500 nm were different in these two matrices, too. Relatively less $Py^{\bullet-}$ radical ions were generated in o-PP as compared with PP.

The influence of temperature on the absorption spectra of Py radical ions for o-PP–Py system is shown in Fig. 3.

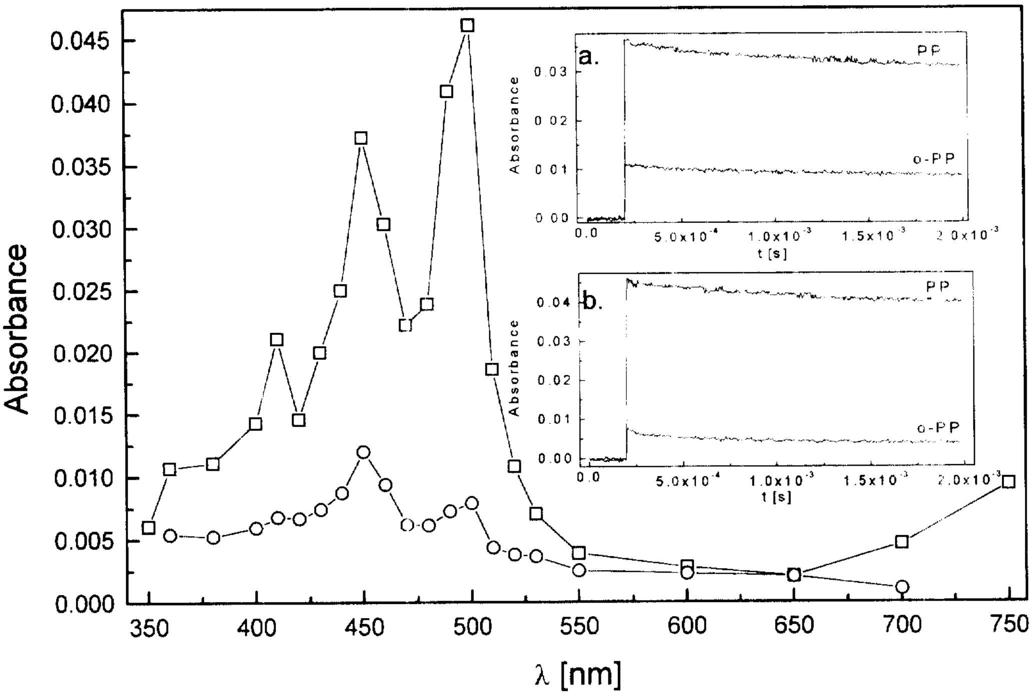

Fig. 2. Optical spectra of pulse irradiated PP–Py (□, [Py] ~ 4.5×10^{-3} mol dm^{-3}) and o-PP–Py (○, [Py] ~ 2.5×10^{-3} mol dm^{-3}) taken 5 μs after the 1 μs pulse at 273 K; ~0.06 cm thick sample. Insets: Absorption-time profiles for these two systems measured at: (a) 500 nm; (b) 450 nm.

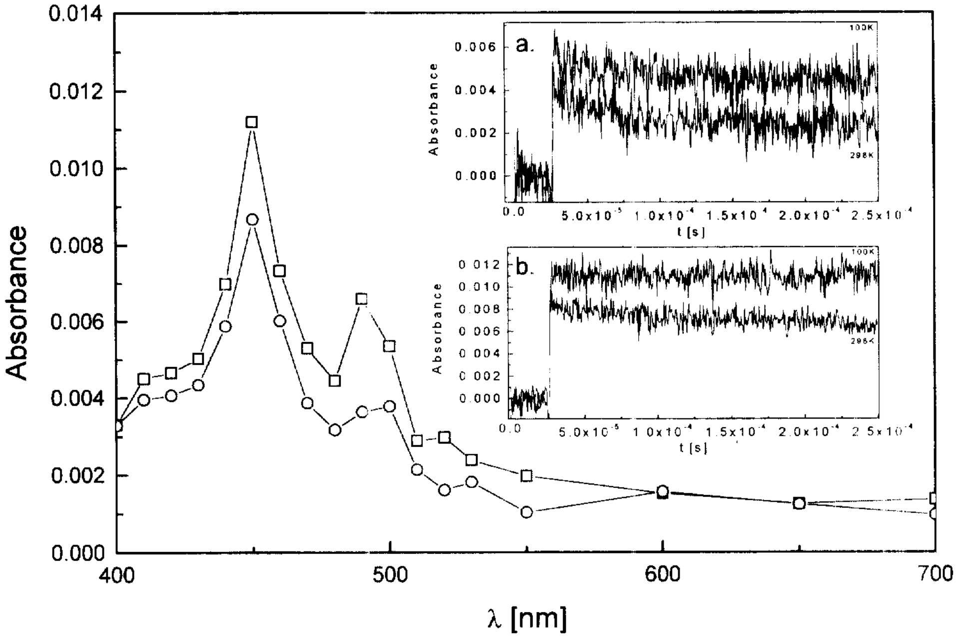

Fig. 3. Influence of temperature on the Py radical ions spectra taken 10 μs after the 1 μs pulse for pulse irradiated o-PP–Py system ([Py] ~ 3×10^{-3} mol dm^{-3}); ○—298 K; □—100 K; 0.065 cm thick sample. Insets: Absorption-time profiles measured at: (a) 500 nm; (b) 450 nm.

The change of temperature from 298 K down to 100 K led to significant increase of Py radical-ions yield measured 10 μs after the 1 μs pulse.

When polymer samples doped with Py were pulse irradiated (17 ns pulse) solute luminescence was found to be produced during and after the pulse. The emission spectra for Py doped samples are shown in Fig. 4. For PP–Py system at room temperature there was strong emission picking at 390 nm assigned to Py monomer fluorescence as it was observed before [21]. In the case of o-PP–Py system, only traces of Py emission were detected under the same experimental condition as for PP–Py film.

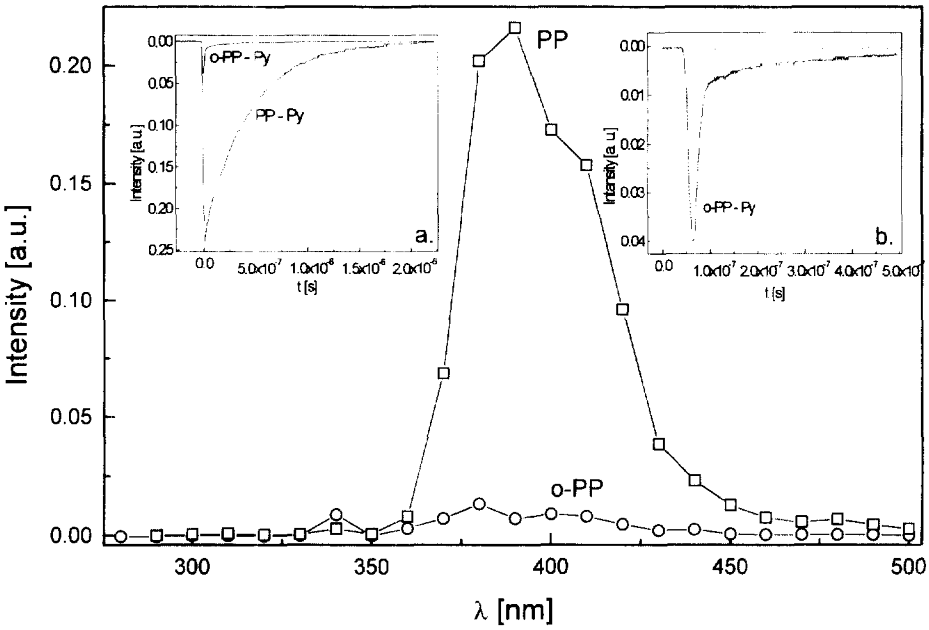

Fig. 4. The room temperature spectrum of emission for pulse irradiated (17 ns pulse) PP–Py (□) and o-PP–Py (○) systems taken 55 ns from the beginning of the pulse ([Py] ~ 4.5×10^{-3} mol dm^{-3} in both matrices. Samples thickness ~ 0.06 cm. Insets: (a) Traces of Py fluorescence decay at 390 nm detected in both matrices; (b) Enlarged trace of Py fluorescence decay curve at 390 nm for o-PP–Py system (shown in (a)). The shape of the pulse depicted as a Čerenkov emission (...) is shown for comparison.

The decay of Py fluorescence in pulse irradiated PP matrix was very well described by the first order kinetics with rate constant equal to 2.32×10^{6} s^{-1}.

Exactly the same value was obtained for laser excited PP–Py system (Fig. 5). The decay of such Py emission generated by laser excitation in o-PP–Py film was faster and was not described by simple first order kinetics. The similar shape of Py emission decay curve was detected for pulse irradiated o-PP–Py system.

The oxidation of the PP generates as a major products hydroperoxides, peroxides and carbonyl groups attached to the polymer chain [5,8–14].

This type of compounds are well known as good electron scavengers [25] hence disappearance of e$_t^-$ absorption in the case of pulse irradiated o-PP matrix seems to be reasonable. Two absorption bands attributed to oxidation product anions were observed for pulse irradiated o-PP film (Fig. 1). The visible band (400 nm–700 nm) can be assigned to car-

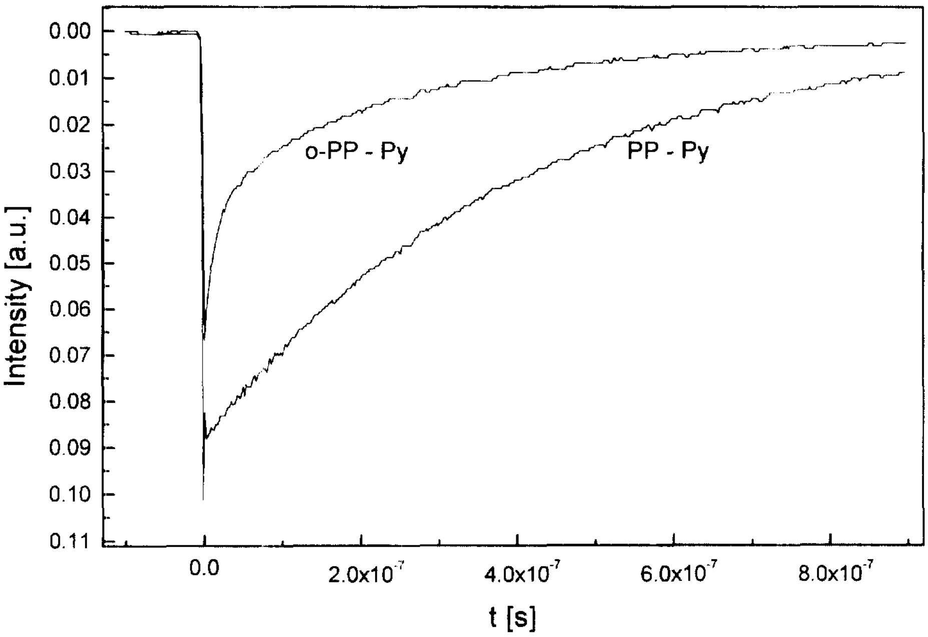

Fig. 5. The Py emission decay curves (390 nm) measured for PP–Py and o-PP–Py system ([Py] ~ 4.5×10^{-3} mol dm^{-3} in both samples, sample thickness ~ 0.006 cm at room temperature. Excitation source-N$_2$ laser, 300 ps pulse. ~ 78 μJ energy in pulse.

bonyl negative ion due to resemblance with acetone molecular anion [26,27]. The UV band (λ_{max} ~300 nm) might be tentatively attributed to peroxide anions.

For the o-PP–Py system, one can observe on a microsecond time scale the scavenging of charges by Py in competition with oxidized matrix itself (Figs. 2 and 3). In general, less Py radical ions were generated in o-PP matrix as compared with PP film. The room temperature rate constants of electron scavenging reactions by Py and oxidized products of PP (represented by model compounds, i.e., acetone, hydrogen peroxides etc.) are rather similar [25]. The lower yield of $Py^{\cdot -}$ in o-PP as compared with PP matrix can be understood assuming that the concentration of oxidized products in o-PP should be locally quite high and the short distance scavenging reaction of e^- with o-PP will be much more probable than with Py at rather low concentration used ($\sim(3 \div 5) \times 10^{-3}$ mol dm^{-3}). Similar explanation can be applied to the positive charge scavenging. After the pulse charge transfer from o-PP matrix, ions to Py was not observed. The acetone ions are reactive species and showed enhanced decay rates in the presence of Py at low concentration [27]. This type positive charge transfer process was not observed even though the gas phase ionization potential of Py was found to be much lower than that of PP oxidized products represented by certain model compounds (acetone, hydrogen peroxide, etc.) [28].

In order to explain such unexpected results, one must assume very fast recombination of PP oxidation products ions which should prevent the charge transfer to Py. In addition, positive carbonyl ions can also react with the neighbouring part of o-PP chain by proton transfer generating, in the end, corresponding radicals although the latter mechanism seems to be less probable [27]. Since the experimental Py radical ions decay curves (Figs. 2 and 3) should be treated as a result of superposition of two processes i.e., Py radical ions decay and Py radical ions generation due to charge transfer, one should also consider that the temperature range (100 K–298 K) used in our pulse radiolysis experiments was not favourable for separation of these reactions.

This part of discussion can be summarized by the reaction (1)–(4).

$$\text{o-PP} - \rightarrow (e^- + h^+ + \text{o-PP}) \rightarrow \text{o-PP}^- + \text{o-PP}^+ \tag{1}$$

where e^- and h^+ denote electrons and positive holes Small fraction of charges escaping rapid charge capture process (1) can be scavenged by Py

$$\text{o-PP}^- + \text{o-PP}^+ \rightarrow \text{o-PP}^* \tag{2}$$

$$e^- + Py \rightarrow Py^{\cdot -} \tag{3}$$

$$h^+ + Py \rightarrow Py^{\cdot +} \tag{4}$$

The observed ratio of absorptions, A, attributed to Py radical ions i.e., $A_{py\cdot +}/A_{py\cdot -}$ was higher for o-PP as compared with PP matrix (Figs. 2 and 3). These results strongly suggested that o-PP matrix was able to react with electrons more efficiently than with positive charges.

The competition between reactions (1) and (3) and (4) was temperature dependent. At low temperature process, (1) was less effective than at room hence, the yield of Py radical ions was found to be higher at 100 K (Fig. 3).

Short distance Py radical ions pairs in PP are able to recombine during the pulse at room temperature giving as a result, Py fluorescence [21]. In the case of o-PP–Py system, very weak Py luminescence was only observed (Fig. 4). Such result can be understood taking into account that in o-PP–Py system less Py ions are generated as compared with PP–Py system (Fig. 2) and in addition, long distance Py radical ion pairs are mainly produced in the former matrix. The energy transfer from excited states, formed as a result of fast recombination of o-PP ions, (reaction (2)), to Py seems to be less probable because of the very short lifetime of these excited states. For example, acetone singlet lifetime was found to be equal only to 1.7 ns [27]. In addition, o-PP matrix was found to quench Py fluorescence. It was clearly seen in Figs. 4 and 5. The decay curves of Py fluorescence in o-PP matrix was not described by simple first order kinetic equation regardless of excitation sources. This result seems to suggest that the quenching mechanism involves the PP oxidation products but not the corresponding ions. Energy transfer from variety of aromatic hydrocarbons (from benzene to coronene including Py) and ketones to di-*tert*-butyl-peroxide, *tert*-butylhydroperoxide and H_2O_2 was observed by Encinas and Lissi [29].

Summing up the results and discussion, one can conclude that the o-PP matrix represent new kind of the system very different from the parent polymer, PP

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