Photo-induced radical formation in ethylene–propylene copolymer by electron spin resonance spectroscopy*

R. P. Singh, R. Mani and S. Sivaram†
Polymer Chemistry Division, National Chemical Laboratory, Pune 411008, India

and J. Lacoste and J. Lemaire
Laboratoire de Photochimie, Moleculaire et Macromoleculaire, URA CNRS 433,
Université Blaise Pascal et ENS Chimie de Clermont-Ferrand, 63177 Aubire Cedex, France
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The photodegradation of heterophasic ethylene–propylene copolymers and their homopolymers has been investigated by the study of hydroperoxide formation, and by electron spin resonance (e.s.r.) and infra-red spectroscopy. On irradiation of polymer films in air at 60°C with a light of wavelength longer than 300 nm, polymer hydroperoxides are formed. The behaviour of peroxyl radicals generated in the samples on irradiation of polymer hydroperoxides with ultraviolet light at −50°C in vacuum has been identified and compared with a combination of e.s.r. and derivatization reactions. From Fourier transform infra-red spectroscopy the structure of peroxyl radicals formed is identified.

(Keywords: radical formation; ethylene–propylene copolymer; electron spin resonance)

INTRODUCTION

Ethylene–propylene (E–P) copolymer is an outstanding material widely used in various industrial fields. Such copolymers may have a range of properties, from stiff thermoplastics to soft elastomers, depending upon the composition of the polymer. Several authors[1,2] have attempted to interpret free radicals produced in polyolefins upon radiolysis; most of the studies have employed very low temperatures in an attempt to freeze out the subsequent reactions of the initial radicals. However, the exact mechanism of photodegradation and radical formation in E–P copolymers has not been fully elucidated. Both the chemical composition of the copolymer as well as conditions of photodegradation are likely to affect the photodegradation processes.

In this paper, we report our results on the effect of u.v. light on the photodegradation of E–P copolymer and the homopolymers of ethylene and propylene by the study of hydroperoxide formation and electron spin resonance (e.s.r.) on free radicals produced after irradiation under vacuum of preoxidized films, with a view to elucidating the mechanism of photodegradation and identifying the macroperoxyl radicals.

EXPERIMENTAL

Materials

Commercial samples of isotactic polypropylene (i-PP); IPCL, Baroda, India), linear low density polyethylene (LLDPE; Du Pont, Canada, Sclair) and heterophasic ethylene–propylene copolymer (EPQ 30R; Himont Italia) were used in this study.

Procedure

The methods of purification, fractionation and sample preparation (~100 μm thick film) have already been reported[3]. The copolymer EPQ 30R was fractionated as fractions A and B (EPQ 30R-A and EPQ 30R-B). The molar percentages of ethylene in the copolymer samples EPQ 30R, EPQ 30R-A and EPQ 30R-B are 15.1, 7.7 and 40.9, respectively. All samples were irradiated in a Pyrex e.s.r. tube at ambient humidity in a SEPAP 12/24 photoirradiation chamber for 140 h at 60°C and at $\lambda \geqslant 290$ nm. The details of this equipment are given elsewhere[3,4]. The preirradiated film (0.012 g) was sealed under high vacuum in a Pyrex e.s.r. tube and inserted in the e.s.r. cavity for irradiation from a 1000 W xenon arc at −50°C. The xenon arc emission was filtered with 305 nm quartz filter to eliminate wavelengths below 305 nm. The distance between the xenon source and the sample was set at 15 cm.

Macromolecular hydroperoxides formed on the photooxidized samples during SEPAP irradiation (140 h) were titrated by iodometry[5] (refluxing in 10:1 isopropanol/acetic acid with excess sodium iodide). The blank reagents were handled in the same way.

$$2ROOH + 2I^- \rightarrow ROH + I_2$$

$$I_2 + I^- \rightarrow I_3^-$$

Any I_3^- formed was measured spectrophotometrically at 355 nm (extinction coefficient of I_3^- assumed to be 25 000 l mol^{-1} cm^{-1}).

The e.s.r. measurements were performed with a Bruker Electron Paramagnetic Resonance 200 instrument equipped with liquid nitrogen temperature-controlled device. Spectra were measured at 12 mW power when peroxyl signals did not saturate. After e.s.r. measurements,

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† To whom correspondence should be addressed

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the sample tube was dropped into liquid nitrogen so that no loss of radicals occurred. It was then reacted with gaseous nitric oxide (NO) for 3–4 h at −78°C and then for 72 h at −20°C in the absence of oxygen to convert peroxyl radicals to their corresponding nitrates/nitrites, which were identified by Fourier transform infra-red (*FT*i.r.) spectroscopy using a Nicolet 800 spectrometer equipped with a Nicplan microscope (liquid nitrogen cooled MCT detector, 128 summations). Spectral subtractions were performed to emphasize changes.

RESULTS AND DISCUSSION

Figure 1 shows plots of the changes in hydroperoxide concentration in the photo-oxidized samples *versus* irradiation time. The hydroperoxides developed linearly in the early stages of photo-oxidation and then quickly reached a photostationary state. The stationary concentration of hydroperoxide observed after 200 h can be accounted for by the partial decomposition of hydroperoxide. In contrast, in the case of LLDPE, EPQ 30R (in Pyrex tube) and EPQ 30R-B, no photostationary state was obtained and a continuous increase in the hydroperoxide concentration was observed. Probably, a longer duration of irradiation is required to attain the photostationary limit.

The photolysis reactions of preirradiated samples explain the loss of hydroperoxide and formation of radical species. The radicals produced from u.v. irradiation (xenon lamp using 305 nm filter) were identified by e.s.r. spectroscopic analysis (followed by *FT*i.r. derivatization) as they do not decay under vacuum at −50°C. *Figure 2* shows a broad pseudo-singlet for i-PP, EPQ 30R-A and EPQ 30R, having a line width at maximum slope, ΔH_{msl}, of 22.5, 21.0 and 20.0 G, respectively. The singlet spectra from irradiated LLDPE and EPQ 30R-B are sharp with ΔH_{msl} of 15.0 and 17.5 G, respectively. These signals are the typical peroxyl radicals, as it is generally expected that alkoxyl radicals are rapidly converted into more stable peroxyl radicals[6] and show no additional feature attributable to alkyl species:

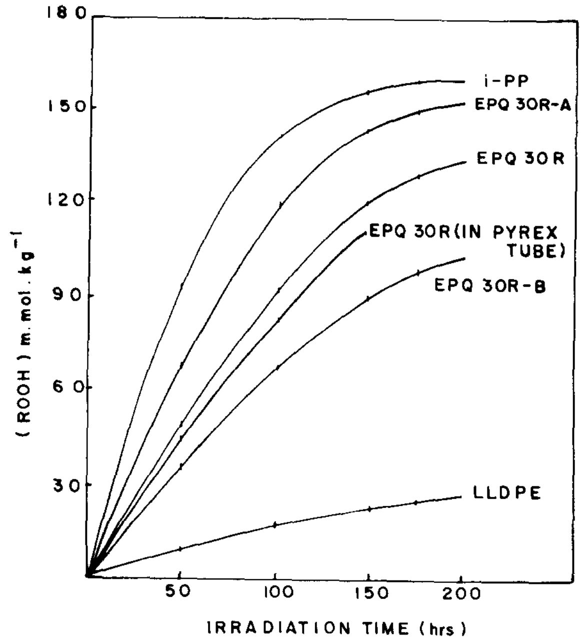


Figure 1 Variations in hydroperoxide contents of 100 μm films irradiated in SEPAP at 60°C

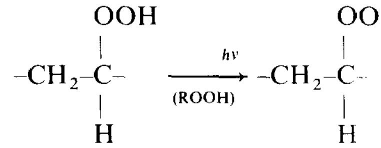
$$\mathrm{ROOH} \xrightarrow[\text{vacuum}]{h\nu} \mathrm{RO^{\bullet}} + {}^{\bullet}\mathrm{OH}$$

$$\mathrm{RO^{\bullet}} + \mathrm{ROOH} \longrightarrow \mathrm{ROO^{\bullet}} + \mathrm{ROH}$$

$${}^{\bullet}\mathrm{OH} + \mathrm{ROOH} \longrightarrow \mathrm{ROO^{\bullet}} + \mathrm{H_2O}$$

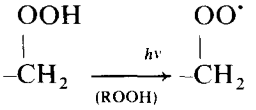
The small ripples visible in the wings of the e.s.r. spectra may result from macroalkyl radicals.

In the absence of oxygen the peroxyl radicals are produced by the photolysis of hydroperoxides already formed in the sample. The study of radical production, at low temperature[7–9] under vacuum, by photolysis of preoxidized polymers has attracted much attention because of the direct implication of the mechanism of initiation and degenerate branching in photo-oxidation of polyolefins. The primary process in preoxidized film under vacuum at −50°C during u.v. irradiation in the present system arises from the decomposition of secondary and tertiary hydroperoxides as:



$$\begin{array}{c}\mathrm{OOH}\\|\\-\mathrm{CH_2}-\mathrm{C}-\\|\\\mathrm{H}\end{array} \xrightarrow[\text{(ROOH)}]{h\nu} \begin{array}{c}\mathrm{OO^{\bullet}}\\|\\-\mathrm{CH_2}-\mathrm{C}-\\|\\\mathrm{H}\end{array}$$

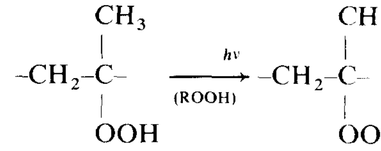
I



$$\begin{array}{c}\mathrm{OOH}\\|\\-\mathrm{CH_2}\end{array} \xrightarrow[\text{(ROOH)}]{h\nu} \begin{array}{c}\mathrm{OO^{\bullet}}\\|\\-\mathrm{CH_2}\end{array}$$

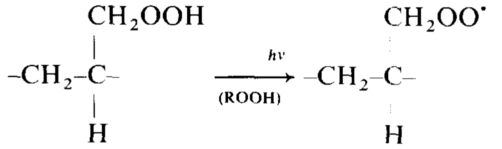
II

In LLDPE, the dominant peroxyl species is proposed to be **I** and several authors[9–11] have identified peroxyl radical **III** as a dominant species in the photolysis of tertiary hydroperoxide of i-PP:



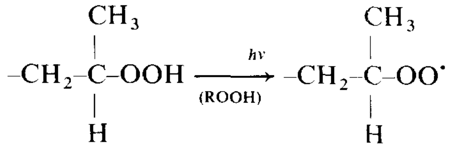
$$\begin{array}{c}\mathrm{CH_3}\\|\\-\mathrm{CH_2}-\mathrm{C}-\\|\\\mathrm{OOH}\end{array} \xrightarrow[\text{(ROOH)}]{h\nu} \begin{array}{c}\mathrm{CH_3}\\|\\-\mathrm{CH_2}-\mathrm{C}-\\|\\\mathrm{OO^{\bullet}}\end{array}$$

III



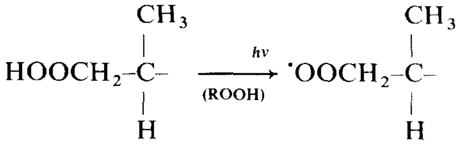
$$\begin{array}{c}\mathrm{CH_2OOH}\\|\\-\mathrm{CH_2}-\mathrm{C}-\\|\\\mathrm{H}\end{array} \xrightarrow[\text{(ROOH)}]{h\nu} \begin{array}{c}\mathrm{CH_2OO^{\bullet}}\\|\\-\mathrm{CH_2}-\mathrm{C}-\\|\\\mathrm{H}\end{array}$$

IV



$$\begin{array}{c}\mathrm{CH_3}\\|\\-\mathrm{CH_2}-\mathrm{C}-\mathrm{OOH}\\|\\\mathrm{H}\end{array} \xrightarrow[\text{(ROOH)}]{h\nu} \begin{array}{c}\mathrm{CH_3}\\|\\-\mathrm{CH_2}-\mathrm{C}-\mathrm{OO^{\bullet}}\\|\\\mathrm{H}\end{array}$$

V



$$\begin{array}{c}\mathrm{CH_3}\\|\\\mathrm{HOOCH_2}-\mathrm{C}-\\|\\\mathrm{H}\end{array} \xrightarrow[\text{(ROOH)}]{h\nu} \begin{array}{c}\mathrm{CH_3}\\|\\{}^{\bullet}\mathrm{OOCH_2}-\mathrm{C}-\\|\\\mathrm{H}\end{array}$$

VI

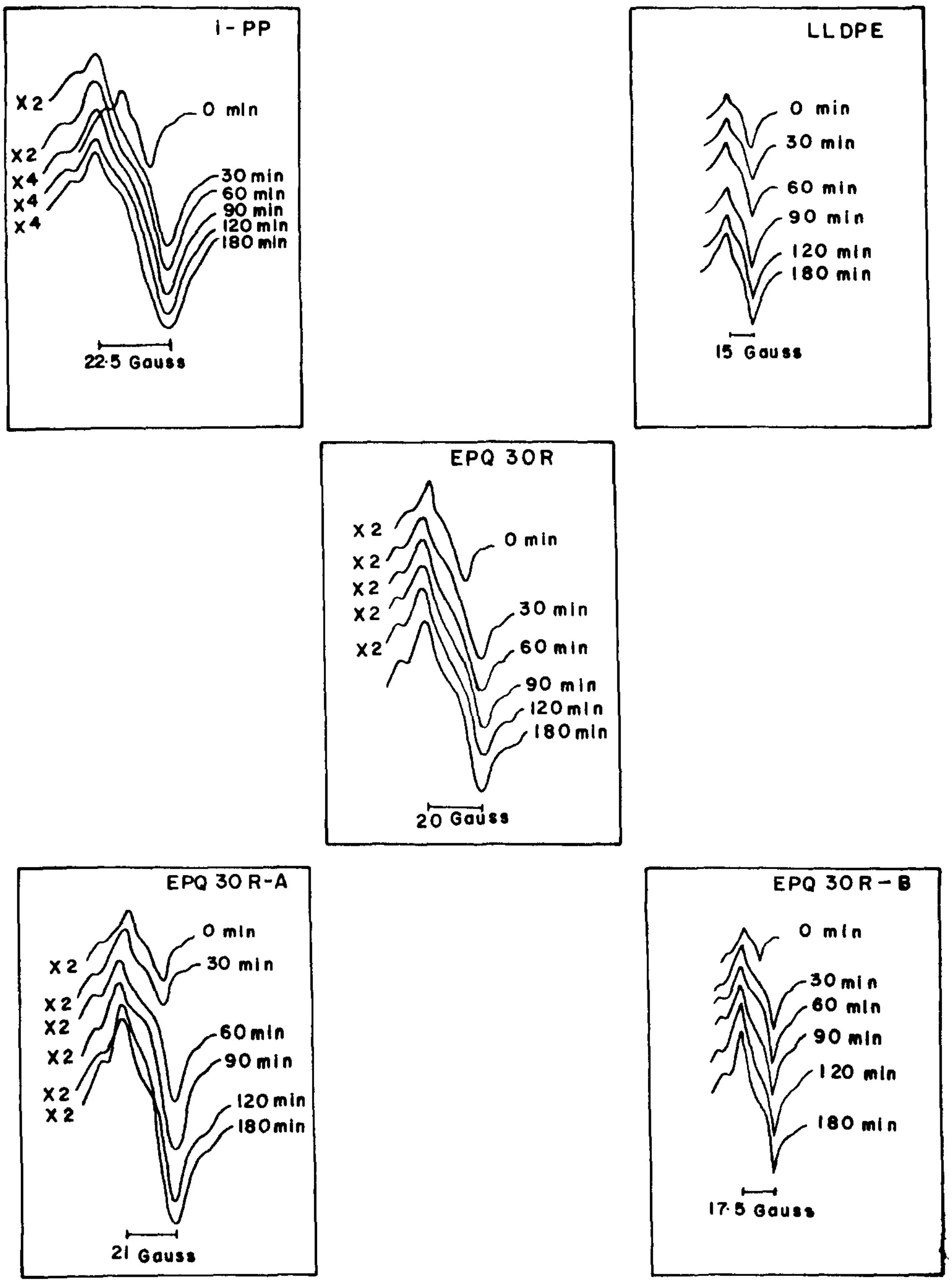


Figure 2 Variations in e.s.r. spectra of preoxidized film in vacuum after u.v. irradiation at −50°C

At −50°C these peroxyl radicals neither propagate nor terminate but accumulate. Longer irradiation at −50°C caused an increase in intensity of the singlet, but a saturation limit is reached at ~180 min, probably due to completion of the photolytic reaction. The saturation curves of the peroxyl radicals produced during irradiation of preoxidized samples were measured under the experimental conditions and the results are shown in *Figure 3*. The peroxyl species yield from the preoxidized sample is ~10 times greater in i-PP than in LLDPE. This confirms the known behaviour that in i-PP a much higher concentration of tertiary hydroperoxides is produced compared to LLDPE photo-oxidation. It is apparent that saturation is reached readily in LLDPE and EPQ 30R-B. The hydroperoxide content of the sample from *Figure 1* resembles quite closely the corresponding values for radicals measured by e.s.r. (*Figure 3*). The results indicate that EPQ 30R and EPQ 30R-A show a similar behaviour to i-PP, whereas EPQ 30R-B peroxyl species production is similar to the behaviour of LLDPE.

The identification of the initial peroxyl radical that actually begins the oxidative chain process is of much greater importance. Although e.s.r. can quantify the free radicals[9] in the solid film, the identification of their precise structure (primary, secondary or tertiary, backbone or chain-end etc.) is possible only by derivatization with NO gas. Once formed, the new end-group resulting from the chain-end rupture should be quite stable, facilitating studies of long-term properties. These peroxyl radicals (ROO$^\bullet$) react with NO gas, which penetrates the solid film by slow diffusion to give the corresponding nitrates/nitrites[9,12,13]:

$$\mathrm{ROO^\bullet + NO \xrightarrow{-20^\circ C} [RO^\bullet + NO_2] \longrightarrow RONO_2}$$

$$\mathrm{RO^\bullet + NO \xrightarrow{-20^\circ C} RNO_2}$$

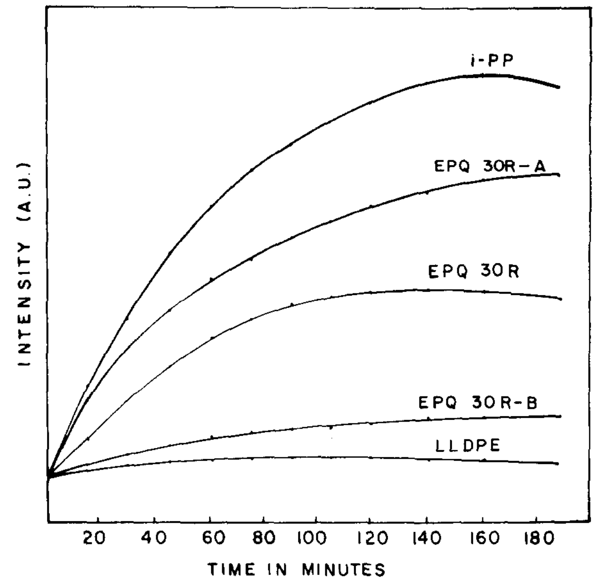


Figure 3 Variations of peroxyl radical concentration in preoxidized film with irradiation time in e.s.r. tube under vacuum at −50°C

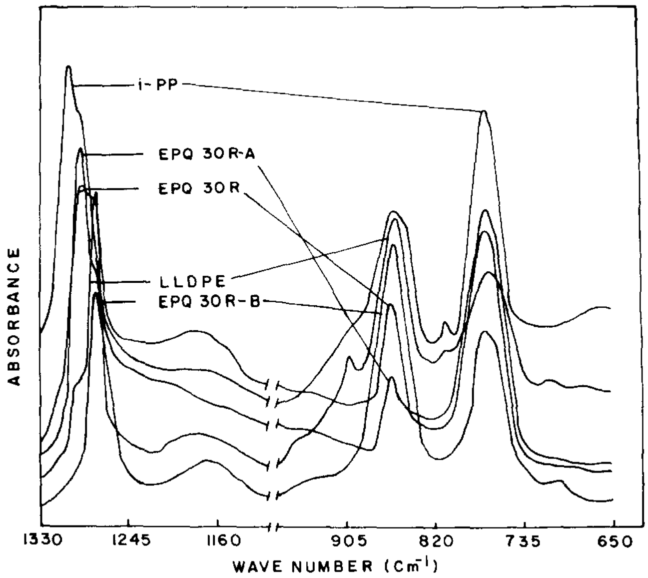


Figure 4 Nitrate products from peroxyl radicals by *FT*i.r. All preoxidized samples were exposed to u.v. photolysis at −50°C in vacuum for 180 min. Spectra were obtained by subtracting the spectrum of the preoxidized film from the corresponding photolysed and NO-treated film

The LLDPE and EPQ 30R-B give dominant isolated secondary nitrate at 1276 cm^{-1}. The tertiary nitrate absorption is quite prominent at 1302 and 1290 cm^{-1} in i-PP, which results from the reaction of NO with ROO$^{\bullet}$ radical at the chain-end and along the backbone of the polymer[14], respectively. The EPQ 30R-A shows tertiary absorption at 1290 cm^{-1}, while EPQ 30R shows a sharp peak at 1290 cm^{-1} and the appearance of secondary nitrate at 1276 cm^{-1}, also due to ethylene content in the sample. The alcohol groups can also react with NO to give nitrites. The alcohol comes from the photolytic reaction:

$$RO^{\bullet} + ROOH \longrightarrow ROH + ROO^{\bullet}$$

$$ROH + NO \longrightarrow RNO_2$$

Tertiary nitrite at 760 cm^{-1} is more prominent in i-PP, EPQ 30R-A and EPQ 30R, whereas secondary nitrate absorption at 860 cm^{-1} is dominant in LLDPE and EPQ 30R-B and the tertiary nitrite peak (760 cm^{-1}) is quite broad. The small secondary nitrite absorption (778 cm^{-1}) is observable in LLDPE and EPQ 30R-B only. The sharp peak at 1631 cm^{-1} is assigned to secondary and tertiary isolated nitrate groups. Isolated nitrate groups are dominant in LLDPE and EPQ 30R-B but in thermoplastic samples (i-PP, EPQ 30R and EPQ 30R-A) this band shows a cluster, which confirms that i-PP forms associated hydroperoxides[15]. These results indicate that EPQ 30R-A generates peroxyl radicals, as does i-PP, whereas EPQ 30R-B, like LLDPE and EPQ 30R, shows an intermediate behaviour with a greater resemblance to i-PP. In addition, separation (deconvolution) is necessary for precise identification, which was affected by spectral subtraction of oxidized samples from the photolysed and NO-treated sample (*Figure 4*).

The peroxyl radical concentration obtained from e.s.r. and their identification by *FT*i.r. are in fairly good agreement. In conclusion, we note that e.s.r. spectroscopy combined with photoirradiation under vacuum at low temperature is an original and very sensitive method for the evolution of hydroperoxide produced from the photooxidation of polyolefins. In addition, the derivatization of peroxyl radicals by NO can be a suitable method to differentiate alkoxyl and peroxyl radicals and therefore for the mechanism of oxidation.

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