

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Photodegradation of Heterophasic Ethylene-Propylene Copolymers in the Solid State

R. P. Singh^a; Ajeet Singh^a

^a Polymer Chemistry Division, National Chemical Laboratory, Pune, India

To cite this Article Singh, R. P. and Singh, Ajeet(1991) 'Photodegradation of Heterophasic Ethylene-Propylene Copolymers in the Solid State', Journal of Macromolecular Science, Part A, 28: 5, 487 – 502

To link to this Article: DOI: 10.1080/00222339108052102

URL: <http://dx.doi.org/10.1080/00222339108052102>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

PHOTODEGRADATION OF HETEROPHASIC ETHYLENE-PROPYLENE COPOLYMERS IN THE SOLID STATE

R. P. SINGH and AJEET SINGH

Polymer Chemistry Division
National Chemical Laboratory
Pune 411008, India

ABSTRACT

The photodegradations of various heterophasic ethylene-propylene (E-P) copolymer films were studied at 30 and 55°C in air for varying time intervals. The photochemical behavior of E-P copolymers is quite different from amorphous polypropylene and polyethylene homopolymers but resembles that of isotactic polypropylene. The nonvolatile products in photooxidized copolymer films have been quantitatively identified by infrared analysis. The kinetics and general oxidation mechanism scheme for E-P copolymer are presented. The identification of γ -lactone is an indication of the importance of an intramolecular back-biting process. The overall functional group distribution is found to differ from that in polyethylene and E-P copolymers.

INTRODUCTION

Many studies on the photodegradation of polyethylene and polypropylene by ultraviolet or visible light [1–6] or heat [7, 8] have received extensive attention during the past decade. The fundamental and practi-

*NCL Communication 4747.

cal aspects of the chemical changes in these polymers in the solid state have been recognized, and it has been observed that the basic reaction in photooxidative degradation is similar to what occurs in thermal oxidative degradation. The important causes of photodegradation and/or thermal degradation of polyolefins are hydroperoxide and ketone or carbonyl group formation. There has been some controversy over whether the hydroperoxide groups or the ketone groups are more effective sensitizers in photooxidative degradation. The photooxidation rates and product distribution of polypropylene and polyethylene films when initiated with UV and γ -irradiation, respectively, have been studied by Carlsson and coworkers [5, 6]. In the complete absence of stabilizers and at controlled rates of radical formation, the polyethylene samples are oxidized at essentially the same rate to give the same degradation products. In their studies they mainly discussed the effects of the chemical nature, concentration, and stability of various additives on the UV stability of polypropylene and polyethylene. In order to improve all aspects of the stability of polymers, a fundamental understanding of the degradation processes involved is essential.

The primary photochemical event in homopolymers and copolymers is the hydroperoxidation [9] which leads to the formation of oxidation products (alcohols, ketones, acids, esters). The chemical scission of the polymeric chains may result from β -scission of polymeric alkoxy radicals, as in polypropylene, and via the Norrish type I and II reactions, characteristic of ketone compounds, as in polyethylene or polypropylene. Although the oxidative phenomenon is restricted to the amorphous regions, the alkyl radicals can be formed both in the amorphous and in the crystalline regions. Decker [10] confirmed that alkyl radicals migrate from the crystalline region to the interfacial zone accessible to oxygen. In the present investigation, photooxidative degradation in the solid phase of various heterophasic ethylene-propylene (E-P) copolymers with different ethylene weight ratios is described. The photooxidation of a heterophasic E-P copolymer has been compared to that of polypropylene and polyethylene homopolymers [1-6]: this study confirms that the photochemical behavior of E-P copolymers is quite different. The photodegradation of ethylene-propylene elastomers, which are typical amorphous polyolefins, has been studied by several workers [9, 11-13] in solution and in solid films, but no attention has been directed toward understanding the photooxidative degradation of heterophasic ethylene-propylene copolymers.

EXPERIMENTAL

Materials

Five grades of heterophasic ethylene-propylene reactor copolymers (from M/S. Himont Italia) of different composition were examined in this work. These grades are designated as EPQ 30R, EPS 30ER, EPT 30R, EPC 40R, and EPF 30R. The manufacturer's specifications are given in Table 1. The antioxidants and other additives were solvent extracted from the samples.

Procedure

Films were made by dissolving the base material in xylene at 70°C, and the solution was homogenized with occasional stirring. The 2-wt% E-P copolymers solution was cast on glass plates and the solvent was evaporated at room temperature and then under vacuum to dryness. The solution cast films were molded between two Teflon sheets into thin films ($\sim 120 \mu\text{m}$) at 170°C by applying 150 kg/cm² pressure for 30 s, using a preheated hydraulic press. The films were quench-cooled in tap water for 5 min.

Photoirradiation was carried out in an accelerated photoaging polychromatic irradiation chamber connected with an atmospheric air supply constructed and calibrated in the laboratory. The irradiation chamber, shown in Fig. 1, has two 400 W high-pressure mercury vapor lamps

TABLE 1. Properties of Different E-P Copolymer Samples

Sample	Wt% ethylene	MFI ^a	Tensile strength, kg/cm ²	Flexural modulus, kg/cm ²	Izod impact, kg·cm/cm
EPQ 30R	9.2	0.82	280	14,000	40
EPS 30ER	6.8	1.51	270	12,000	30
EPT 30R	13.2	3.48	260	13,000	04
EPC 40R	7.4	7.00	290	13,000	14
EPF 30R	8.2	13.00	290	14,000	12

^aMelt flow index.

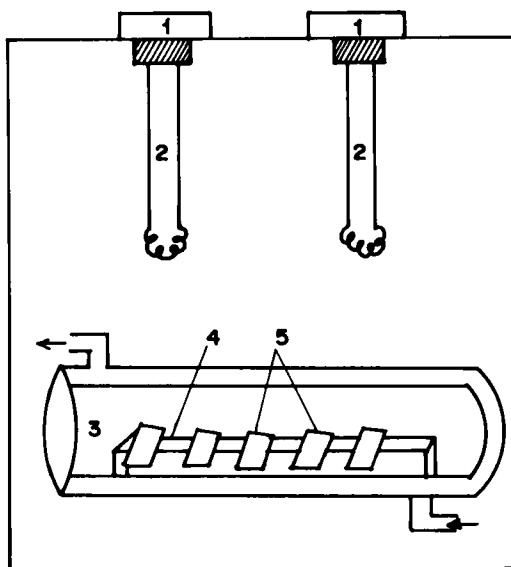


FIG. 1. Diagram of irradiation chamber. (1) Choke, (2) 400 W mercury vapor lamp, (3) Pyrex cylindrical reactor, (4) stand for films, (5) films.

whose glass casing was removed. The lamps are located at the center of the chamber. Radiation of wavelengths shorter than 290 nm were eliminated by a Pyrex glass cylindrical reactor. The temperature of the films in the reactor was controlled to $\pm 2^\circ\text{C}$ by the circulation of water in the reactor. The dried E-P copolymer films ($\sim 120 \mu\text{m}$ thickness) were irradiated with polychromatic light ($\lambda > 290 \text{ nm}$) for different time intervals (100, 200, 300, 400, and 500 h) at 30 and 55°C . The samples were irradiated uniformly on a metal support. The intensity of the radiation was determined by using potassium ferrioxalate actinometry [14] of $1.662 \times 10^{-8} \text{ Einstein} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ ($10 \times 10^{15} \text{ quanta} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$).

Characterization

E-P copolymer films were irradiated with polychromatic light ($\lambda > 290 \text{ nm}$) in an air chamber at 30 and 55°C in a cylindrical Pyrex reactor with a metal support that fitted directly onto the sample holder of a Perkin-Elmer 599B infrared spectrophotometer. The mounted films were withdrawn from the chamber at different photooxidation times, and

their infrared spectra were recorded. The extent of photodegradation was followed by monitoring the build-up in the concentration of the nonvolatile hydroperoxide and carbonyl absorption regions in the spectra at 3400 and 1722 cm^{-1} , respectively.

RESULT AND DISCUSSION

The photodegradation of E-P copolymer films was followed by infrared spectroscopy: the absorption frequencies of the photooxidative degradation products were examined in three main regions.

The carbonyl region (1850–1550 cm^{-1}) showed several overlapping absorption bands, as is the case for most olefinic polymers. This region is broad, indicating a mixture of different functional groups. The bands at 1712, 1738, and 1780 cm^{-1} can be assigned to carboxylic acids, ketones, esters, and lactones. Vinylidene-type unsaturation, observed at 1640 cm^{-1} , results from disproportionation during photodecomposition of polypropylene units. For all five samples, these absorption peaks were more prominent at 55°C and at longer periods of irradiation. The development of the peak at 1640 cm^{-1} was seen only at longer irradiation times. However, these unsaturated groups were more precisely observed at 888 cm^{-1} (out-of-plane vibration of the C–H bond). Of particular interest is the resolution of the band at 1780 cm^{-1} , which was assigned to γ -lactone. It was found that the amount of γ -lactone formed during photodegradation was negligible for polyethylene but significant for polypropylene [13]. We observed a significant amount of aldehyde groups in our studies since the C–H stretching frequency at 2730 cm^{-1} was present due to oxidation of the isotactic polypropylene unit which develops with irradiation time. It is evident from the infrared spectra that the samples do not behave differently in many aspects since the compositions do not differ significantly. The infrared spectra of EPQ 30R, EPS 30ER, EPT 30R, EPC 40R, and EPF 30R are given in Fig. 2. The changes in the absorption bands of these photooxidized samples bear a strong resemblance to those observed in isotactic polypropylene films submitted to the same oxidative conditions. The degradation is a maximum in EPQ 30R and a minimum in EPF 30R, both at the same temperature, while the other samples showed intermediate behavior. This is in accord with the manufacturer's results that EPQ 30R has the lowest melt flow index (MFI) (0.82) while EPF 30R has the highest MFI (13.00); this means that EPQ 30R has the highest molecular weight

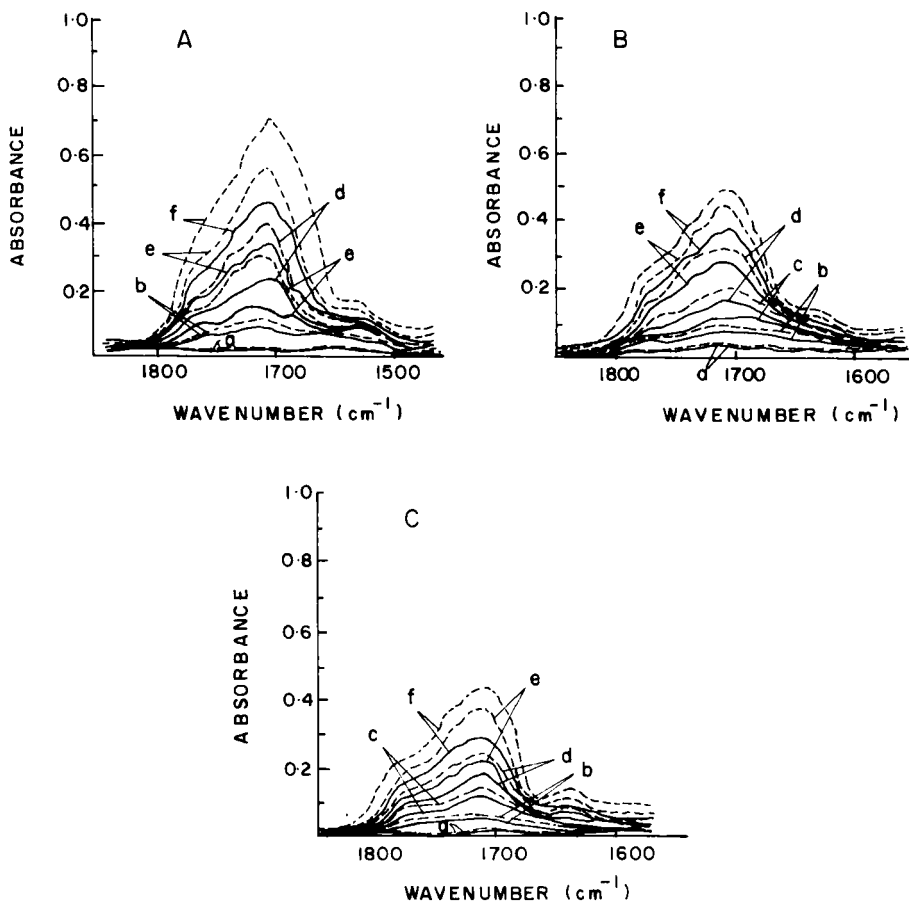


FIG. 2. IR spectra in the 1550–1850 cm^{-1} range of 120 μm thick E-P copolymer films irradiated for various times ($\lambda > 290 \text{ nm}$) at 30 (—) and 55°C (---). (A) EPQ 30R, (B) EPS 30ER, (C) EPT 30R, (D) EPC 40R, (E) EPF 30R. (a) 0 h, (b) 100 h, (c) 200 h, (d) 300 h, (e) 400 h, (f) 500 h.

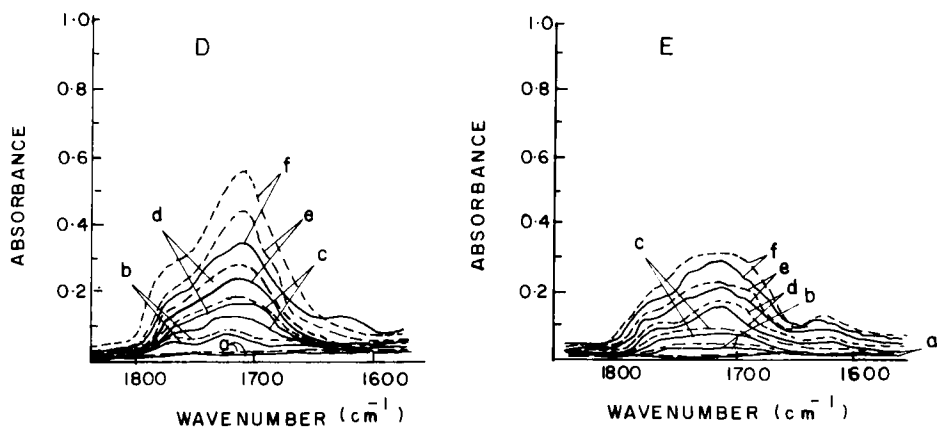


FIG. 2 (continued).

whereas EPF 30R has the lowest, with the other grades having intermediate molecular weights.

A broad hydroxyl absorption region ($3700\text{--}3200\text{ cm}^{-1}$) with a maximum peak at 3400 cm^{-1} during photoirradiation appeared in all samples (Fig. 3): this band is due to the neighboring intramolecular hydrogen-bonded hydroperoxides and alcohols. A medium intensity band developed at 3615 cm^{-1} , due to an isolated hydroxyl band in a tertiary alcohol, did not appear in polypropylene or polyethylene. Hydrogen-bonded hydroperoxides (3420 cm^{-1}) and associated alcohols (3380 cm^{-1}) were also detected, with the hydrogen-bonded hydroperoxides developing faster in all samples. Isolated tertiary alcohols and associated tertiary alcohols indicate the contribution of isolated polypropylene units, whereas associated hydroperoxides are formed on the polyethylene segments. Note that at high propylene contents (propylene $> 45\%$), since hydroperoxidation does not occur at isolated propylene units but rather on ethylene sequences, free tertiary hydroperoxides are not seen at all. At high propylene contents, polypropylene sequences can be formed and tertiary hydrogen-bonded hydroperoxides appear: such hydroperoxides are decomposed into ketone groups which are not photochemically converted into vinyl groups as in polyethylene (the carbon atom located at the β -position of the carbonyl group is substituted).

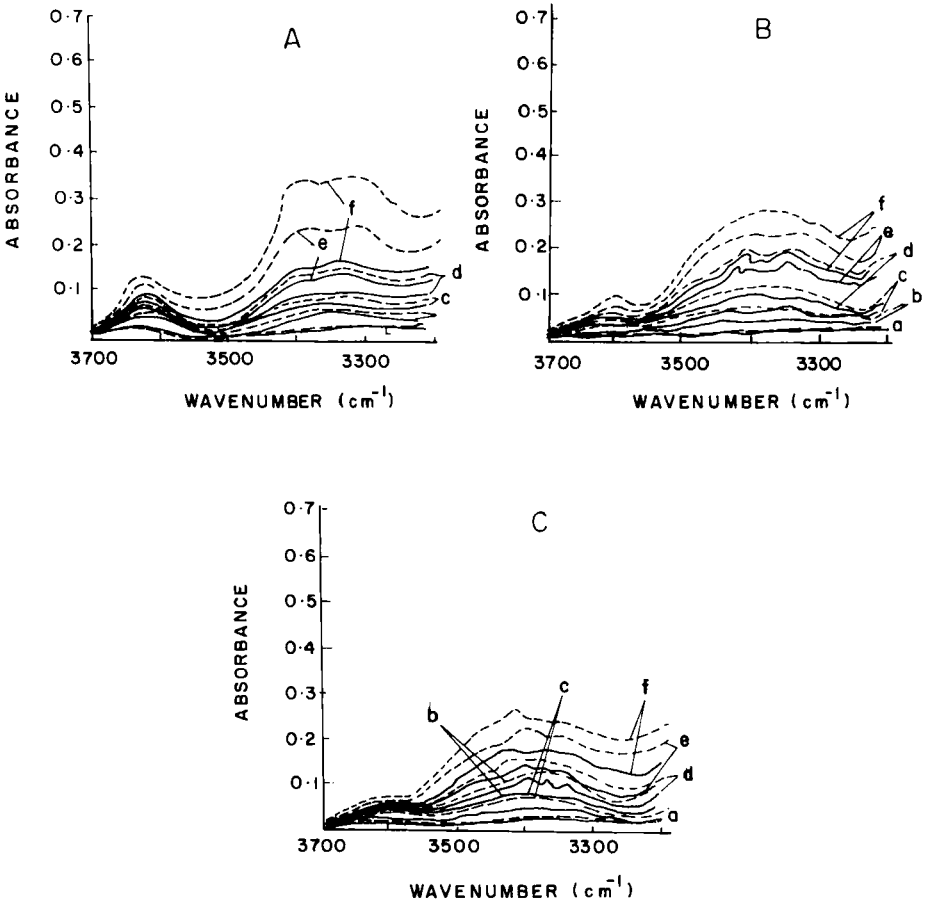


FIG. 3. Hydroxyl region ($3200\text{--}3700\text{ cm}^{-1}$) of $120\text{ }\mu\text{m}$ thick E-P copolymer films irradiated for various times at $30\text{ }^\circ\text{C}$ (—) and $55\text{ }^\circ\text{C}$ (---). (A) EPQ 30R, (B) EPS 30ER, (C) EPT 30R, (D) EPC 40R, (E) EPF 30R, (a) 0 h, (b) 100 h, (c) 200 h, (d) 300 h, (e) 400 h, (f) 500 h.

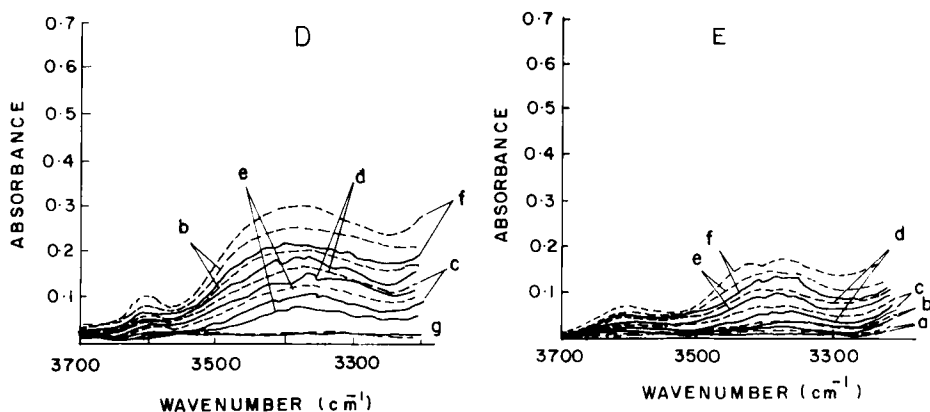


FIG. 3 (continued).

Figure 4 presents the changes in absorbance of free tertiary alcohol (3615 cm^{-1}) as a function of the changes in the absorbance at 3400 cm^{-1} . In early stages of the photooxidation, formation of free tertiary alcohol occurs in parallel with the appearance of hydrogen-bonded alcohols and hydroperoxides. However, on longer exposure times the free tertiary alcohols reach a stationary concentration, indicating that the free hydroxylated compounds gradually change into hydrogen-bonded associations. Under our experimental conditions we have not detected the formation of isolated hydroperoxides absorbing at 3550 cm^{-1} in any of the five samples during photooxidation degradation.

In the region of the infrared spectra corresponding to the out-of-plane vibration of the C-H bond due to unsaturation ($800\text{--}1000\text{ cm}^{-1}$) for all the samples, an increase was observed in the vinylidene end groups ($>\text{C}=\text{CH}$) at 888 cm^{-1} and in the vinylene chain ($-\text{CH}=\text{CH}-$) at 968 cm^{-1} . These unsaturations are believed to be formed by Norrish type II photoreactions of the ketones. Vinylidene unsaturation is developed as a result of disproportionation during the decomposition of polypropylene units. The vinylidene absorption (888 cm^{-1}) was quite prominent and increased with irradiation time in all the samples. The development of band at 1640 cm^{-1} also indicates the formation of the unsaturated vinylidene group due to disproportionation of the propylene unit. The vinyl

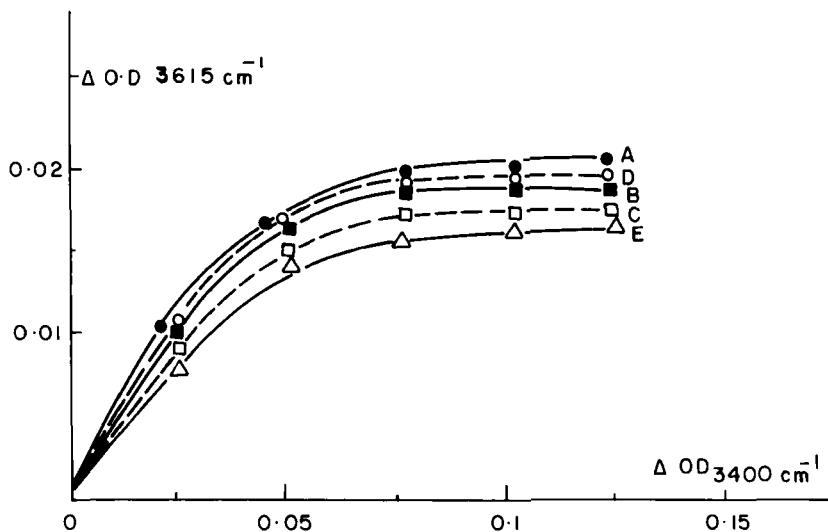


FIG. 4. Variation of absorbance at 3615 cm^{-1} versus absorbance at 3400 cm^{-1} for E-P copolymer films at 55°C . (A) EPQ 30R, (B) EPS 30ER, (C) EPT 30R, (D) EPC 40R, (E) EPF 30R.

unsaturation content (909 cm^{-1}) remained steady over the whole exposure time at both temperatures.

The copolymer samples showed an induction period of about 25 h at 30°C and 10 h at 55°C , after which hydroperoxide and carbonyl groups began to accumulate, but in the case of EPF 30R the induction period was 40 and 20 h at 30 and 55°C , respectively.

Kinetic Aspects of Photodegradation

The isolated hydroperoxides were not observed in photooxidized samples of E-P copolymer at 30 or 55°C . Only hydrogen-bonded hydroperoxides absorbing around 3400 cm^{-1} (prominent at 3350 and 3420 cm^{-1}) were detected in all five samples. As shown in Fig. 5, the hydroperoxide absorbance increases as a function of exposure time at both temperatures. It is also apparent from the curves that the hydroperoxidation rates are highest in EPQ 30R and lowest in EPF 30R, while in the other samples the rates are intermediate.

Variations in the absorbance of carbonyl photoproducts at 1722 cm^{-1}

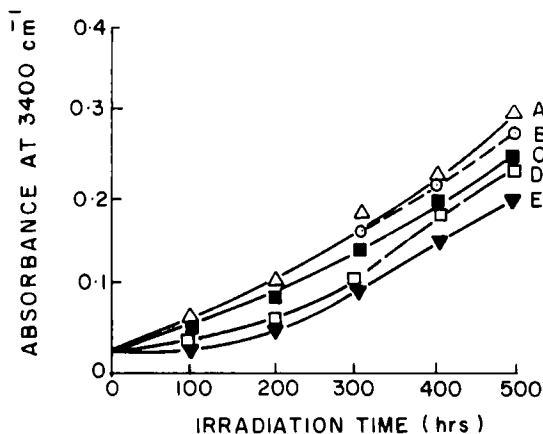


FIG. 5. Variation of absorbance at 3400 cm^{-1} as a function of irradiation time ($\lambda > 290\text{ nm}$) of $120\text{ }\mu\text{m}$ E-P copolymer films at 55°C . (A) EPQ 30R, (B) EPS 30R, (C) EPT 30R, (D) EPC 40R, (E) EPF 30R.

are plotted as a function of the irradiation time in Fig. 6. The rate of carbonyl group formation is independent of the extent of the oxidation up to 500 h irradiation. In EPF 30R, the changes in the corresponding rates are the lowest. In Fig. 7 the changes in the absorbance of vinylidene groups (888 cm^{-1}) are plotted as a function of the irradiation time. Again, the rate of formation of vinylidene groups is higher in EPQ 30R. It was also found that at higher temperature the absorbance at 1722 cm^{-1} increases at a faster rate than the variation in absorbance of the vinylidene groups. At the initial stages of photooxidation, the amount of hydroperoxides is higher than that of ketones. However, the amount of carbonyl quickly builds up after the initial period, while the level of hydroperoxide concentration remains relatively low. This indicates that the primary photoproducts are hydroperoxides which decompose to produce ketones. The decomposition of one hydroperoxide group was found to give rise to more than one carbonyl group. The rate of photodecomposition of hydroperoxide did not follow unimolecular kinetics and was a function of the carbonyl content of the copolymers [15]. Thus, the hydroperoxides are the primary absorbing species that initiate the subsequent photochemistry.

Based on these results and kinetic evidence, the photodegradation behavior of E-P copolymer resembles that of isotactic polypropylene;

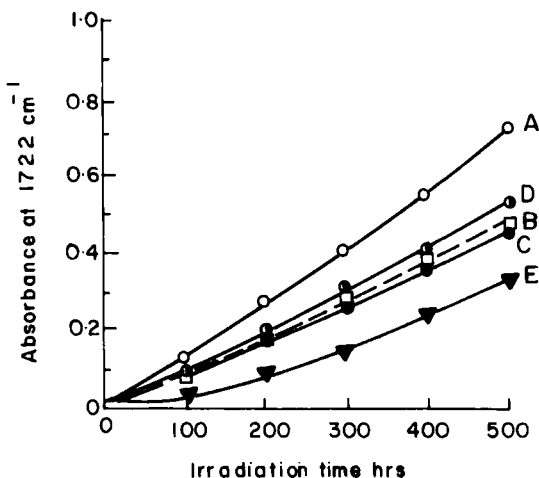


FIG. 6. Variation of carbonyl content versus irradiation time of $120 \mu\text{m}$ E-P copolymer films at 55°C . (A) EPQ 30R, (B) EPS 30ER, (C) EPT 30R, (D) EPC 40R, (E) EPF 30R.

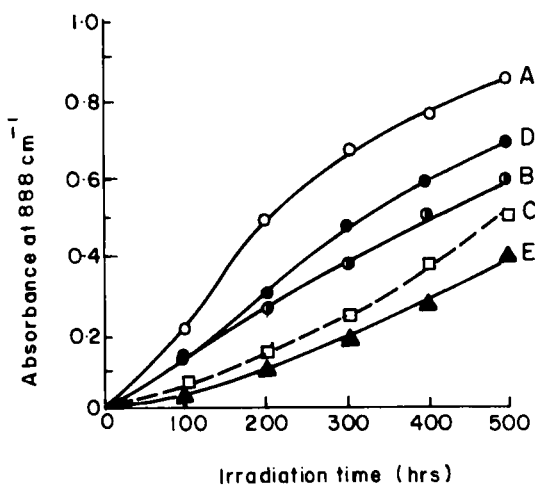


FIG. 7. Variation of vinylidene absorbance (888 cm^{-1}) as a function of irradiation time of $120 \mu\text{m}$ E-P copolymer films at 55°C . (A) EPQ 30R, (B) EPS 30ER, (C) EPT 30R, (D) EPC 40R, (E) EPF 30R.

for example, in the distribution of carbonyl compounds (ketones, acids, and esters). The rate of formation of carbonyl compounds absorbing at 1715 cm^{-1} (ketones + acids) increases because of higher propylene content. The rate of formation of vinyl-type unsaturation appears only in some cases, which is a clear indication of the photodegradation of isotactic polypropylene. In isotactic polypropylene the Norrish type II process occurring in the intermediate ketones cannot lead to vinyl-type unsaturation, whatever the structures of the ketones formed.

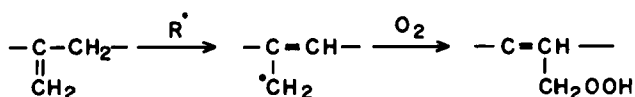
Mechanism of Photodegradation

The photodegradation of polyolefins is defined by initiation, propagation, and termination steps [16]. In the case of E-P copolymer, the tertiary and secondary hydroperoxides are photochemically decomposed into chain ends and main-chain ketones (Scheme 1) [17].

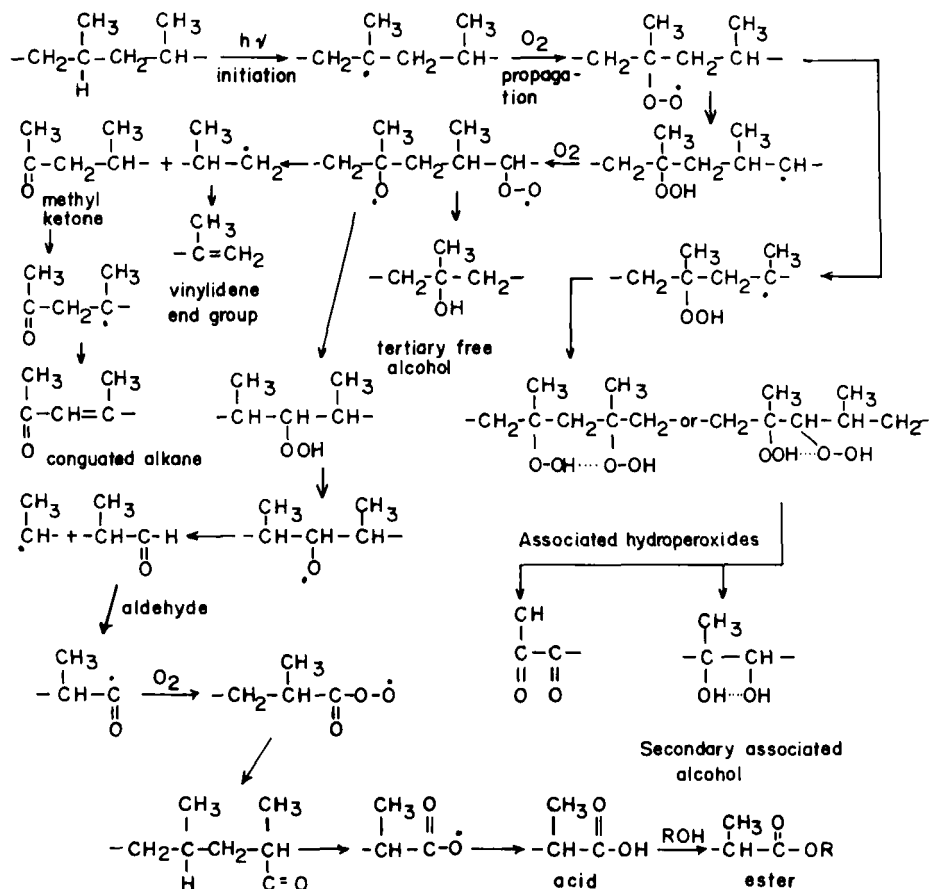
The decomposition of hydroperoxide led to chain-scission with the conversion of hydroperoxide groups on the backbone to ketone groups at the chain ends.

The ketones are converted into vinylidene unsaturation by a Norrish type II process. The chain-end ketone can be converted into acetone or a vinylidene group. The conjugated alkene absorbance band was the strongest after the film was exposed at 55°C . Here, only the hydroperoxides formed at the propylene units were included since the thermal oxidation at a tertiary center on a polypropylene chain is expected to be many times faster than that at the methylene carbon of polyethylene. However, the main source of this increased photodegradability must be due to the presence of hydroperoxides in the former sample. Cheng et al. [18] reported that secondary hydroperoxides found in photodegraded samples are essentially due to the decomposition of ethylene blocks in the copolymer. Any radical formed in the E-P copolymer during polychromatic irradiation would either abstract a hydrogen atom or add to an unsaturated group. It is expected that abstraction of a secondary hydrogen atom would prevail over the abstraction of a tertiary carbon.

Abstraction Mechanism



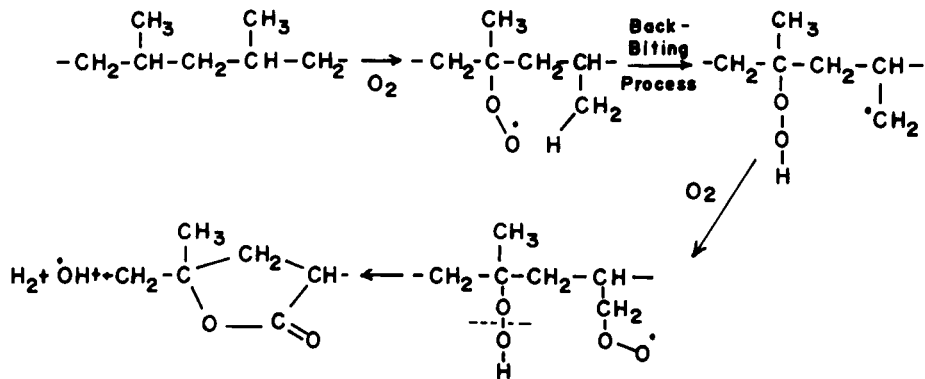
Formation of primary hydroperoxides implies the simultaneous generation of vinylidene and hydroperoxide groups, in accordance with our



SCHEME 1.

results. Tertiary hydroperoxides were not detected in the present investigation, and therefore an addition mechanism is not possible.

The determination of γ -lactone (1780 cm^{-1}) as a major product in the photooxidized E-P copolymer is important because it lends evidence to an intramolecular back-biting mechanism [19] during oxidation (Scheme 2). γ -Hydrogen abstraction by the back-biting peroxy radical is believed to be the key step in the eventual production of the γ -lactone.



SCHEME 2. Back-biting process.

ACKNOWLEDGEMENT

The authors are extremely grateful to Dr. S. Sivaram, Deputy Director and Head, Polymer Chemistry Division, National Chemical Laboratory, Pune, India, for stimulating suggestions and discussions.

REFERENCES

- [1] J. Lemair and R. Arnaud, in *Polymer Photochemistry*, Vol. 5 (N. S. Allen, ed.), Elsevier, London, 1984, p. 243.
- [2] N. S. Allen (ed.), *Degradation and Stabilization and Poly-olefins*, Elsevier, London, 1983.
- [3] B. Ranby and J. F. Rabek, *Photodegradation, Photo-oxidation and Photostabilization of Polymers*, Wiley, New York, 1975, p. 121.
- [4] G. Gueskens, F. Debie, M. S. Kabamba, and G. Nedelkos, in *Polymer Photochemistry*, Vol. 5 (N. S. Allen, ed), Elsevier, London, 1984, p. 313.
- [5] D. J. Carlsson, D. W. Gratton, T. Suprunchuk, and D. M. Wiles, *J. Appl. Polym. Sci.*, **22**, 2217 (1987).
- [6] D. J. Carlsson, G. Bazan, S. Chmela, and D. M. Wiles, *Polym. Degrad. Stab.*, **19**, 195 (1987).
- [7] M. Iring, T. Kelen, and F. Tudos, *Makromol. Chem.*, **175**, 467 (1974).
- [8] T. Tsuchiya and K. Sumi, *J. Polym. Sci., Pt. A-1*, **7**, 1599 (1969).

- [9] J. Lacoste, R. P. Singh, J. Boussand, and R. Arnaud, *J. Polym. Sci., Polym. Chem. Ed.*, **25**, 2799 (1987).
- [10] C. Decker, *Makromol. Chem.*, **178**, 2969 (1977).
- [11] R. P. Singh, J. Lacoste, R. Arnaud, and J. Lemaire, *Polym. Degrad. Stab.*, **20**, 49 (1988).
- [12] G. Gueskens and M. S. Kabamba, *Ibid.*, **11**, 69 (1982).
- [13] S. K. L. Li and J. E. Guillet, *Macromolecules*, **17**, 111 (1984).
- [14] J. G. Calvert and N. J. Pitts, Jr., *Photochemistry*, Wiley, New York, 1966.
- [15] M. Iring, T. Kelen, F. Tudos, and Zs.Leszlo-Hedvig, *J. Polym. Sci., Polym. Symp.*, **57**, 89 (1976).
- [16] R. Chandra and R. P. Singh, *Makromol. Chem.*, **181**, 1637 (1980).
- [17] R. Arnaud and J. Lemaire, *Polym. Degrad. Stab.*, **15**, 205 (1986).
- [18] H. A. Cheng, F. C. Schilling, and F. A. Bovey, *Macromolecules*, **9**, 363 (1976).
- [19] J. Lacoste, R. Arnaud, R. P. Singh, and J. Lemaire, *Makromol. Chem.*, **189**, 651 (1988).

Received March 28, 1990

Revision received November 25, 1990