

Specific Characteristics of Infrared Spectra of Irradiated γ -Polypropylene

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SYNOPSIS

Nonvolatile products have been identified that arise through γ -irradiation in isotactic polypropylene by Fourier transform infrared (FTIR) analysis. The γ -irradiation was performed in the air with doses varying between 20 and 1200 kGy, for a dose rate of 800 Gy/h. The contour lines of FTIR absorption bands of carbonyl groups at different region of the cross section of an irradiated sample have been determined. The carbonyl groups arise from the concentration of esters or ketones, carboxylic acids, and γ -lactones, but their structure is different for different doses. We have also investigated the degradation of irradiated polypropylene by using FTIR mappings. Dust particles of irradiated brittle polypropylene have also been studied. The gel fraction has been determined for different doses of irradiation, and the relation between the moment of the appearance of the gel and disappearance of the carbonyl groups has been made evident. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Isotactic polypropylene is a semicrystalline polymer with three morphologically distinct regions: crystallites, amorphous region, and surface boundaries. Because of its high crystallinity and its high melting point, polypropylene presents good thermal resistance, good rigidity, and resistance to solvents. The crosslinking and scission occur in irradiated polypropylene and both in proportion to dose. The presence of oxygen greatly affects the radiative degradation; polypropylene, with its numerous oxidation-susceptible tertiary carbons, oxidizes much more quickly than polyethylene.

Normally, the polymer contains small amounts of impurities: concentrations of vinylidene groups, and quantities of carbonyl, hydroxy, and hydroperoxy groups. The chemical changes in these polymers in the solid state have been recognized, and it has been observed that the important causes of degradation are hydroperoxide and ketone or carbonyl formation.¹ Thus, Luongo² shows that in the process of oxidation of polypropylene, the first region of in-

terest is (4000–3000) cm^{-1} , corresponding to hydroxy groups.

Later, the bands in the carbonyl region appear, from 1850 to 1650 cm^{-1} . The typical —C=O bands due to aldehydes, esters, and ketones were merged into a single band between 1710 and 1750 cm^{-1} . The acid —C=O band was the first to form and remained the strongest during and after oxidation. According to Carlsson,³ the carbonyl groups were reported to result from concentration of esters or acids and γ -lactones. For the polypropylene irradiated in air, the concentration of carbonyl groups increases with the irradiation dose, with a subsequent tendency toward stabilization.⁵ The stabilization process is due to the limited diffusion rate of the oxygen within the sample. Although the oxidative phenomenon is restricted to the amorphous regions, the alkyl radicals can be formed both in the amorphous and the crystalline regions. Decker⁴ confirmed that alkyl radicals migrate from the crystalline region to the interfacial zone accessible to oxygen.

In the present investigation, radiative oxidation degradation in the solid phase of γ -irradiated polypropylene is described. The first objective is to make evident the composition of the field of carbonyl at

different doses of irradiated polypropylene in dust particles, as well as the influence of the irradiation dose over isotacticity. The second objective is to analyze Fourier transform infrared (FTIR) mappings contour lines at different doses of irradiation. The existence of the reticular phenomenon has been made evident, as have the dose at which the appearance of the gel is noted and the existence of a relation between the appearance and disappearance of the carbonyl groups.

EXPERIMENTAL PROCEDURES

The samples selected for the study were commercial isotactic polypropylene chipped and compression molded into sheets of 1.8-mm thickness. Samples were irradiated with Cs^{137} - γ ray at doses of 20–1200 kGy. The irradiation was performed by an irradiation equipment of 0.71, Gammator model M38-2, executed by Radiation Machinery Corporation. The dose rate measured by the Fricke dosimeter was 0.8 kGy/h; a variance of 5% in the radiation absorption was accepted. All irradiated samples were kept in the presence of air at room temperature (Fig. 1).

The gel content was determined by means of a soxhlet extractor, using xylene; samples were exposed to refluxing xylene close to its boiling point. Extraction was carried on until the samples attained constant weight; the extraction time was at least 72 h. The gel fraction was calculated by the following equation:

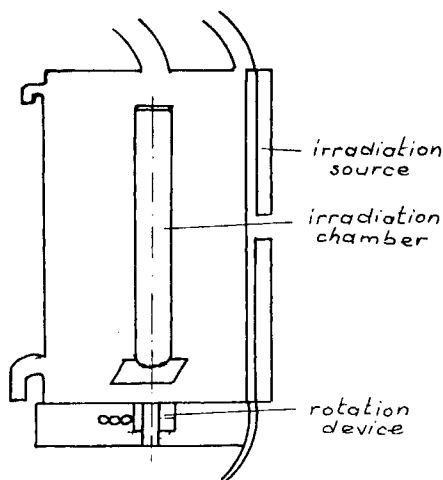


Figure 1 Gammator model M38-2, Cs^{137} - γ ray, irradiation chamber 0.71. The dose rate was 0.8 kGy/h.

$$\text{Gel fraction} = W/W_i$$

where W_i is the initial weight of sample (g) and W is the weight after soaking in the solvent (g).

To obtain the spectrum, the samples were conveniently cut and had the thickness of 10, 20, and 40 μm . All the spectra were recorded on a 50-FTIR Nicolet spectrometer.

RESULTS AND DISCUSSION

Carbonyl Region and Isotacticity

The degradation of polypropylene is defined by initiation, propagation, and termination steps. One of the first products of degradation are hydroperoxyde groups. The decomposition of hydroperoxyde groups led to chain scission, with the conversion of hydroperoxide groups on the backbone to ketone groups at the chain ends. In the case of the spectrum made by us, we have not noted the existence of the hydroperoxide groups. This disappearance is due to the fact that the spectrum made by us was registered a long time after the irradiation.

The carbonyl region from 1850 to 1650 cm^{-1} presents different bands at different doses of irradiation. Thus, at 20 kGy we noted the appearance of the band 1736 cm^{-1} assigned to the ketone group or ester, as well as the band 1716 cm^{-1} assigned to the group corresponding to carboxylic acid [Fig. 2(a)]. At 100 kGy, the intensity of these bands grows a great deal. At this dose, the existence of γ -lactone groups (1774 cm^{-1}) has been identified. The identification of γ -lactones is a sign of the importance of an intramolecular back-biting process⁶ [Fig. 2(b)].

At high doses of irradiation (1200 kGy), γ -lactones disappear, while the concentration of the group 1736 cm^{-1} grows a lot. Surprisingly, the concentration of the carboxylic acid at 1200 kGy is reduced [Figs. 2(c) and (d)]. In fact, at all doses at which we have made measurements, the strongest band is the ketone or ester band.

Through irradiation, polypropylene becomes a brittle material. That is why while cutting the samples, dust particles of irradiated brittle polypropylene were noted. The composition of the carbonyl region of dust particles is different from that of the samples of polypropylene (Fig. 3), with the band of carboxylic acid being, in this case, stronger than the bands of ester or γ -lactone.

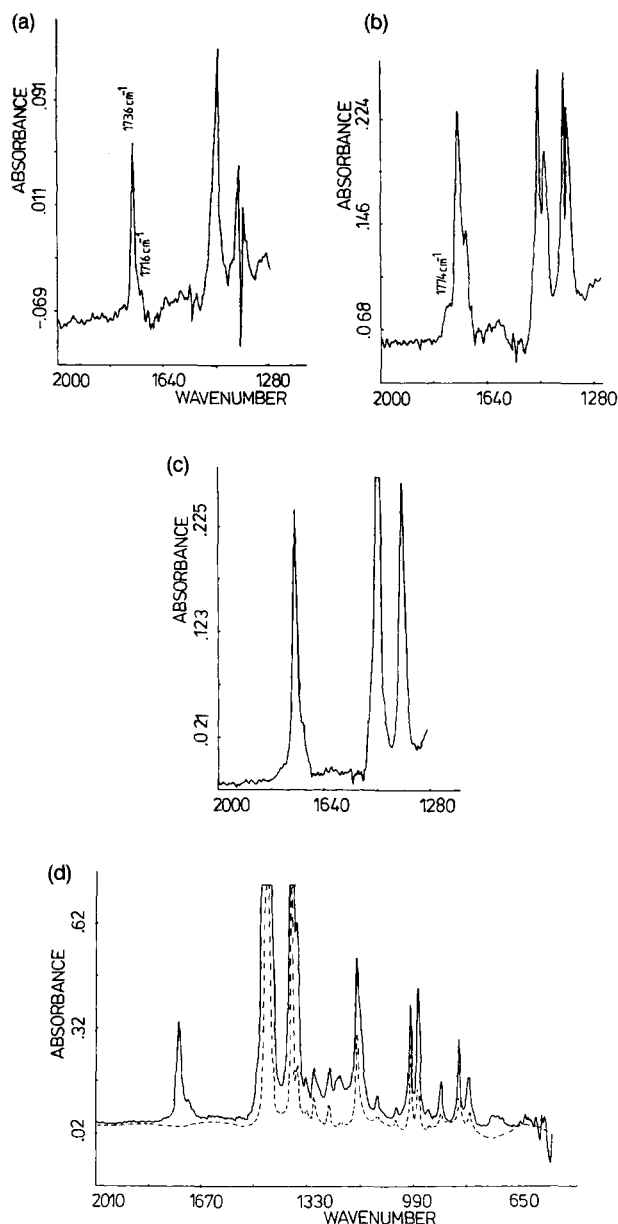


Figure 2 (a) The infrared spectra for the irradiated PP at 20 kGy, appearance of the band 1736 cm^{-1} and of the band 1716 cm^{-1} . (The absorbance for PP 0.20 kGy, less absorbance for nonirradiated PP.) Thickness of the samples was $40\text{ }\mu\text{m}$. (b) The infrared spectra for the irradiated PP at 100 kGy, appearance of the band 1774 cm^{-1} . (Absorbance for PP 100 kGy, less absorbance for nonirradiated PP.) Thickness of the samples was $40\text{ }\mu\text{m}$. (c) The infrared spectra for the irradiated PP at 1200 kGy, disappearance of the band 1774 cm^{-1} . (The absorbance for PP 1200 kGy, less absorbance for nonirradiated PP.) Thickness of the samples was $40\text{ }\mu\text{m}$. (d) The infrared spectra for the irradiated PP at 1200 kGy (continuous curve) and for nonirradiated PP (noncontinuous curve). Thickness of the samples was $20\text{ }\mu\text{m}$.

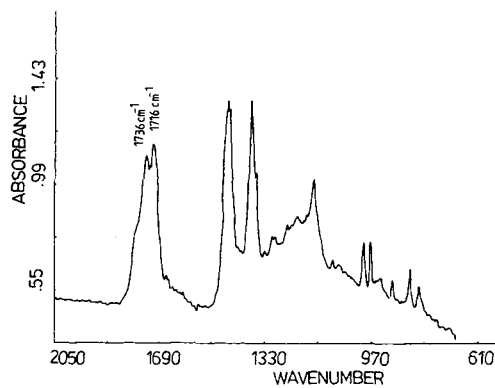


Figure 3 The infrared spectra of dust particles of irradiated PP at 1200 kGy.

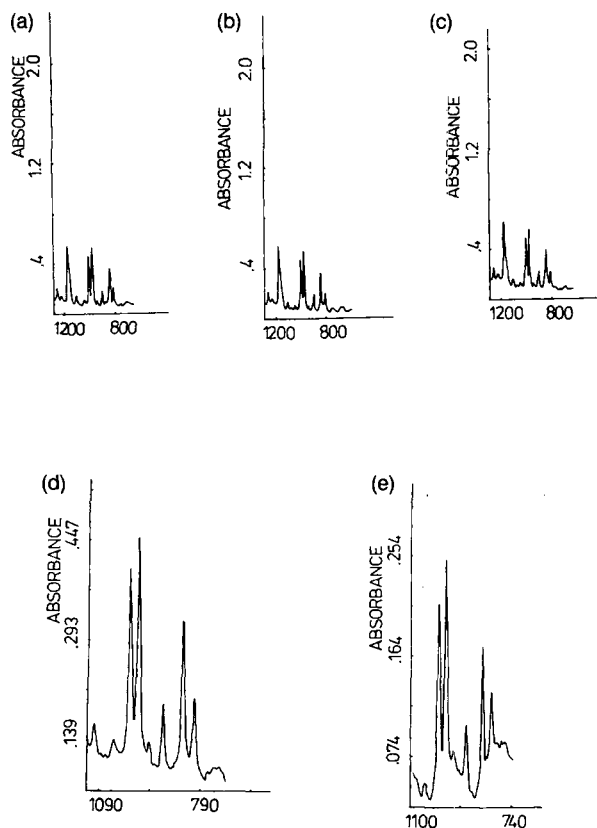


Figure 4 Comparison between the domain of isotacticity of nonirradiated and irradiated PP. (a) The domain of isotacticity of nonirradiated PP, thickness $40\text{ }\mu\text{m}$. (b) The domain of isotacticity of irradiated PP, 20 kGy, thickness $20\text{ }\mu\text{m}$. (c) The domain of isotacticity of irradiated PP, 100 kGy, thickness $40\text{ }\mu\text{m}$. (d) The domain of isotacticity of irradiated PP, 1200 kGy, thickness $40\text{ }\mu\text{m}$. (e) The domain of isotacticity of irradiated PP, 1200 kGy, thickness $20\text{ }\mu\text{m}$.

One cannot understand the phenomenon produced in isotactic irradiated polypropylene if the variation of its crystallinity is not taken into account. Thus, Thomlison and Kline⁷ were among the first who have demonstrated, by differential scanning calorimetry, that irradiation of an isotactic polypropylene to a dose of 6000 kGy lowered the crystallinity to 73% of its original value.

If it is considered that the variation of polypropylene crystallinity is the same as the variation of its isotacticity, then it may be determined through the ratio of the bands 995/974, simultaneously with the ratio of bands 842/810 as well as the intensity of the band 895 cm^{-1} .²

In case of the spectrum made by us [Figs. 4 (a), (b), (c), (d)], these bands do not present significant variations. Thus, crystallinity did not change because the irradiation doses are still low. Similar results have been obtained in case of polyethylene, in which differential scanning calorimetry (DSC) measurements of melting endotherm have indicated that the enthalpy of fusion of polyethylene is unaffected by low doses (0–2000 kGy) but decreases after higher doses.⁸

The same bands appear and are approximately in the same ratio in the case of dust particles. The ratio 995/974 presents a slight increase, which shows a slight growth of crystallinity in dust particles (Fig. 3). This is proof of the fact that the tearing of the particles has been produced from the

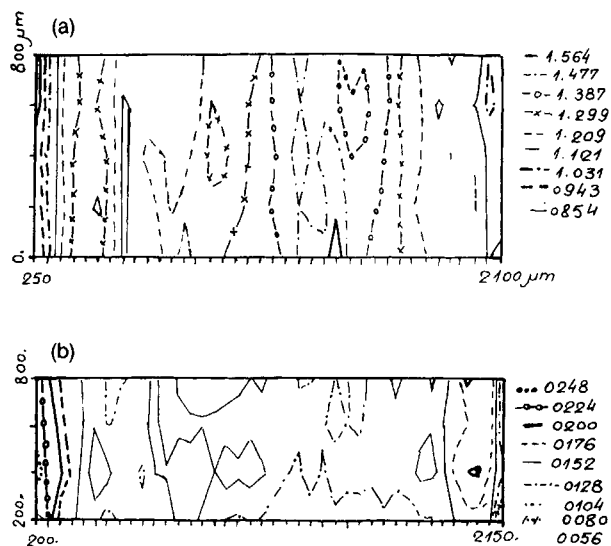


Figure 5 (a) and (b) FTIR mappings for the interval $(1740-1790) \text{ cm}^{-1}$ for irradiated PP, 20 kGy. (a) $R = (A_{1740} - A_{1790}) / (A_{2723} - A_{2694})$; (b) $A_{1740} - A_{1790}$.

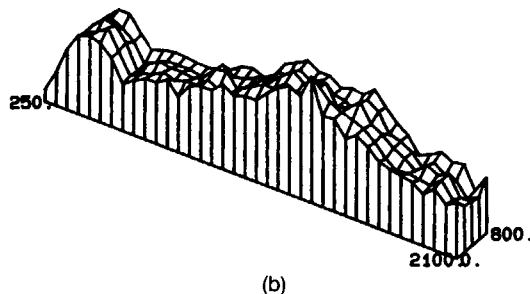
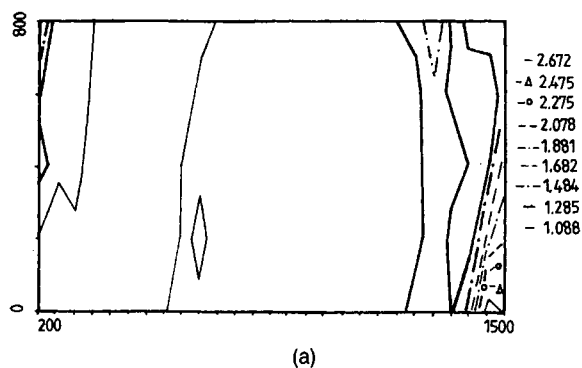


Figure 6 FTIR mappings for the interval $(1740-1820) \text{ cm}^{-1}$ for the interval $(1740-1820) \text{ cm}^{-1}$ for 100 kGy. (a) $R = (A_{1740} - A_{1820}) / (A_{2723} - A_{2694})$; (b) $A_{1740} - A_{1820}$.

amorphous regions, which exist at the limit of the crystalline domains.

FTIR Mappings

To make evident and clarify the changes produced through irradiation, FTIR mappings at different doses of irradiation have been registered, in which interesting changes have been obtained. Effectuation of mappings for the interval $1740-1790 \text{ cm}^{-1}$, which is the domain of esters and γ -lactones, showed the existence of several profiles at the dose of 20 kGy [Figs. 5 (a) and (b)]. Dense profiles which appear

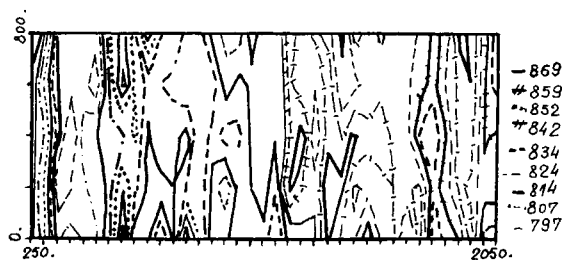


Figure 7 The isotacticity at 20 kGy, $R = (A_{998} - A_{985}) / (A_{974} - A_{985})$.

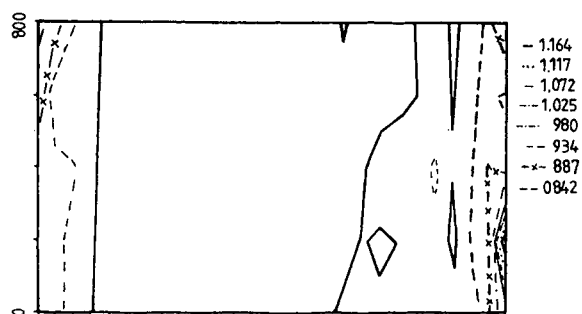


Figure 8 The isotacticity at 100 kGy, $R = (A_{998} - A_{985}) / (A_{974} - A_{985})$.

at 20 kGy show that irradiation has produced, until this dose, many changes of the abovementioned groups; while at 100 kGy we noticed the appearance of some rare profiles and a uniformity of their distribution [Figs. 6(a) and (b)].

This latest observation shows that at this dose a stabilization of the phenomenon has been produced, in comparison with 20 kGy. In the registration we performed, we took into account the variation of absorbance due to thickness, through determination of the difference ($A_{2723} - A_{2694}$). The profiles which show the variation of isotacticity at the doses of 20 kGy and 100 kGy confirm these assertions. Isotacticity has been determined from the ratio $R = (A_{998} - A_{985}) / (A_{974} - A_{985})$. Again, at 20 kGy one can notice the existence of several profiles which show several changes, although isotacticity varies in a limited interval [Fig. 7]. At 100 kGy the obtained profiles are again much rarer and crystallinity is more uniform.

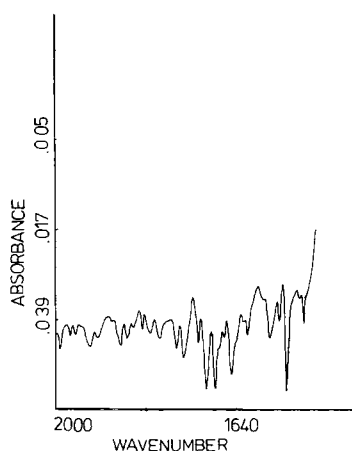


Figure 9 The disappearance of carbonyl groups at the gel point (about 50 kGy). Thickness of the samples was 40 μm .

Table I Gel Content and IR Spectral Changes of Polypropylene Irradiated Samples (40 μm)

| Dose (kGy) | 0 | 20 | 54 | 100 | 1200 |
|---------------|----|-------|----|-------|-------|
| ΔA | 0 | 0.126 | 0 | 0.182 | 0.258 |
| % Gel content | ND | ND | 1% | 10% | ND |

ΔA = difference between the absorbance from carbonyl groups of irradiated and nonirradiated PP. ND = Nondetected.

In this case, too, the variations of isotacticity are produced in a limited interval (0.842 – 0.795), but with a slight lowering of values [Fig. 8]. To make evident the changes in the interval 20–100 kGy, measurements have been made for an intermediary dose of 54 kGy.

Determination of the Gel and Infrared Spectrum at 54 kGy

It is known that simultaneously with the intense degradation processes produced in irradiated isotactic polypropylene (phenomena which are accentuated in irradiation in air), the phenomenon of reticulation, a result the appearance of the gel, is produced. There have been determinations of the gel fraction at doses of 20, 54, 100, and 1200 kGy. Simultaneously, there has been a correlation between the concentration of the carbonyl groups and the gel fraction (Table I). We suggest that the quantity of carbonyl groups declines sharply at the gel point, which was about 50 kGy for our samples [Fig. 9]. This result is similar to the results of Veselovskii.⁹ The variation in the concentration of carbonyl groups is also similar to the variation of concentration of carbonyl groups in irradiated polyethylene, determined by the C^{13} nuclear magnetic resonance (NMR) method.¹⁰

Analyzing FTIR mappings at the dose 54 kGy in the domain 1740–1790 cm^{-1} , one can observe the negligible values of the absorption, which confirms

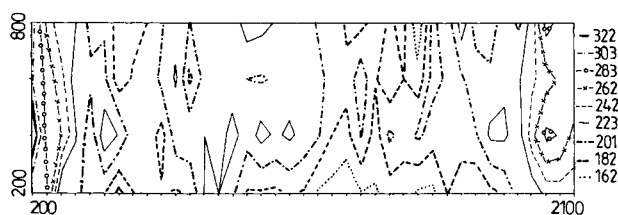


Figure 10 FTIR mappings for the interval (1740–1790) cm^{-1} for irradiated PP, 54 kGy. $R = (A_{1740} - A_{1790}) / (A_{2723} - A_{2694})$.

the negligible concentration of the carbonyl groups (Fig. 10). The appearance of the gel at 100 kGy explains the stability and the small number of profiles at this dose.

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REFERENCES

1. J. H. Adams, *J. Polym. Sci.*, **A1**, 1077 (1970).
2. J. P. Luongo, *J. Appl. Polym. Sci.*, **9**, 302 (1960).
3. D. J. Carlsson and D. M. Wiles, *J. Macromol. Sci. Chem.*, **C14**, 65 (1976).
4. C. Decker, *Makromol. Chem.*, **178**, 2969 (1977).
5. D. Gavrilá and J. Paun, *J. Radioan. and Nucl. Chem.*, **125**, 243 (1988).
6. R. P. Singh and A. Singh, *J. Macromol. Sci.-Chem.*, **A28**, 487 (1991).
7. J. N. Thomlison and D. E. Kline, *J. Appl. Polym. Sci.*, **11**, 1931 (1967).
8. J. H. O'Donnel and A. K. Whittaker, *Radiat. Phys. Chem.*, **39**, 209 (1992).
9. R. A. Veselovskii, S. S. Leshchenko, and V. L. Karpov, *Polym. Sci. USSR*, **1**, 881 (1968).
10. J. C. Randall, in *Crosslinking and Scission in Polymers*, O. Guvern, Ed., (NATO, ASI Series, Kluwer Academic Publishers), 1990, p. 57.

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