Infrared Spectra of Irradiated Polyethylene

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INTRODUCTION

Recent reports in the literature have shown that high energy radiation can seriously modify the physical properties of polymers.[1-3] Since changes in physical properties reflect radiation-induced chemical changes, a knowledge of the reactions that occur on irradiation would contribute to our ability to modify or direct the effects of ionizing radiation.

In this paper, a number of these chemical changes and structural rearrangements are identified by infrared spectroscopy from which certain reaction mechanisms can be postulated.

EXPERIMENTAL DETAILS

The samples selected for this work were DYNK, a branched, high pressure polyethylene produced by Union Carbide Co. and Marlex, a linear and highly crystalline polyethylene made by Phillips Petroleum Co. Neither sample contained any antioxidants.

Solution-crystallized linear polyethylene, hereafter referred to as single crystals, was prepared by collecting the suspension that forms on cooling a boiling, dilute solution of the polyethylene in xylene and thermostating it at 85°C.

These crystals were collected by two different methods. In the first method, the fine flakes of polyethylene crystals were allowed to settle slowly on a sintered glass disk under suction. This required several hours, and a thick cake formed which was dried in a vacuum oven at 40°C. The second method consisted of filtering the suspension of fine flakes rapidly on a large Büchner funnel under suction. This required only a few minutes and resulted in a compact film which was also dried in a vacuum oven at 40°C.

All the samples were prepared for infrared analysis by hot molding into films 3–5 mils thick. The infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer using NaCl optics. All samples were irradiated in a beam of 1 m.e.v. electrons from a Van de Graaff generator. In the vacuum irradiations, prior to electron bombardment, the samples were sealed in evacuated thin-walled ($1/2$ mm.), pyrex tubes following prolonged pumping at 10^{-6} mm. Hg.

RESULTS AND DISCUSSION

A. Bulk Polymer

In Figure 1 are shown the infrared spectra of the branched polyethylene (DYNK), before and after irradiation in vacuum and in air. Strongly absorbing *trans* type unsaturation (CH=CH) bands at 964 cm.$^{-1}$ appear in both the vacuum- and air-irradiated sample spectra. Vinylidene decay on irradiation is shown by the decrease in the R_1R_2C=CH_2 band at 888 cm.$^{-1}$.
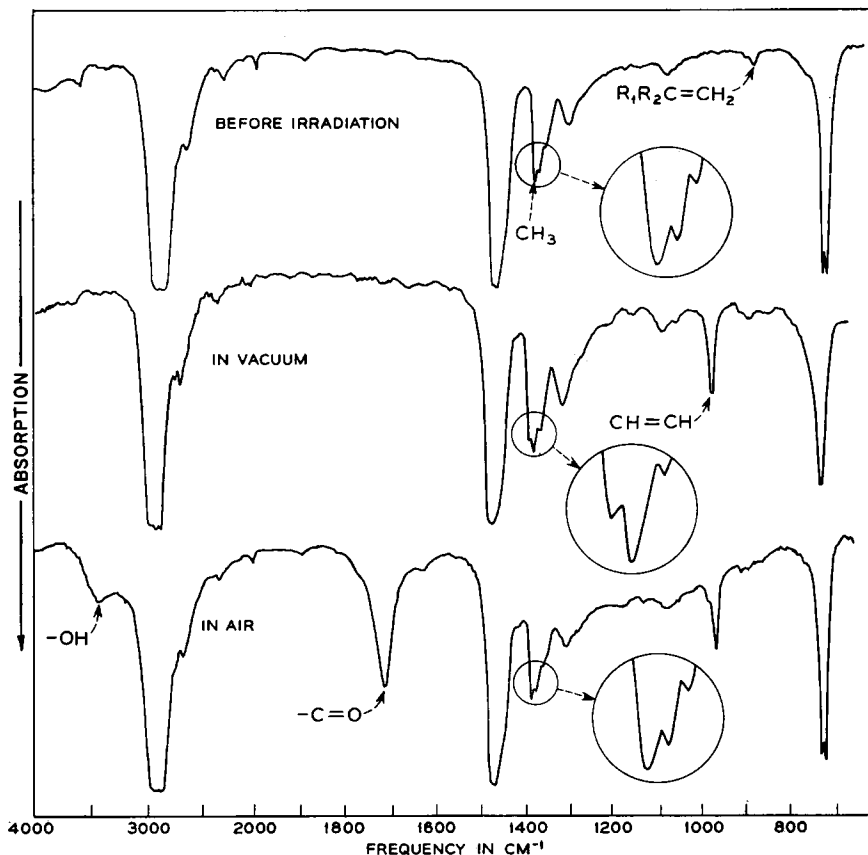

Fig. 1. The effect of irradiation (500 MR) in air and in vacuum on branched polyethylene.

Irradiation in vacuum produces a significant decrease in the methyl (—CH$_3$) content (1373 cm.$^{-1}$), whereas in the bombardment in air, there appears to be only a negligible decrease in —CH$_3$, if any. In addition, a comparison of the 720–730 cm.$^{-1}$ doublet shows that only the 720 cm.$^{-1}$ component remains in the spectra of the vacuum sample, whereas there is

only a slight decrease of the 730 cm.$^{-1}$ component in the air-irradiated sample. Additional evidence of structural changes are shown in the spectra of the air-irradiated sample. Here, both —OH and C=O bands appear, and there is a general depression of the spectrum background from 1300 to 900 cm.$^{-1}$
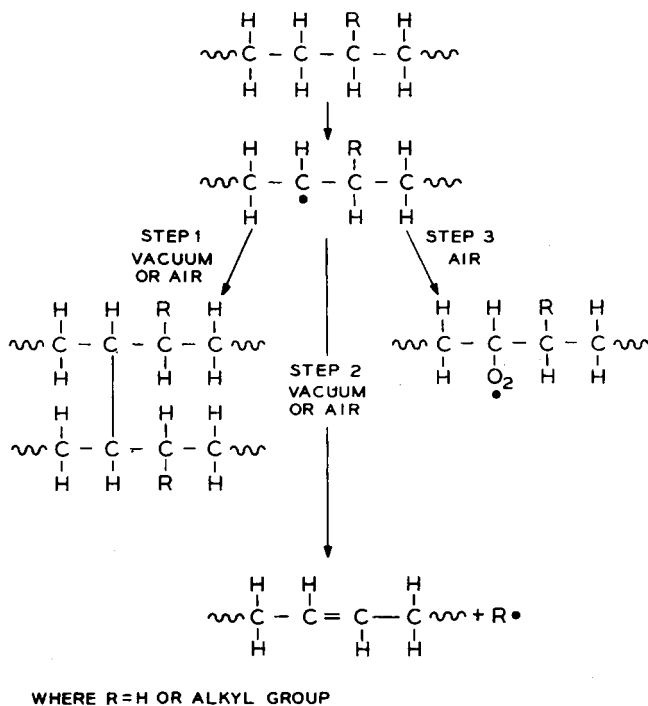

Fig. 2. Postulated reaction mechanism in irradiated branched polyethylene.

A number of these spectral changes can be explained with the aid of Figure 2. That C—H fracture is one of the major effects of irradiation is evidenced by the large amount of hydrogen evolved during irradiation.[2] Moreover, the decrease in the solubility of polyethylene[4] and the increase in *trans* unsaturation on irradiation in air or vacuum indicates that the resultant free radicals may stabilize by crosslinking (Fig. 2, step 1), or by the formation of unsaturation (step 2). In air (step 3), when the C—H bond is broken, the radical may be attacked by oxygen, and then carbonyl, hydroxyl, and other oxygenated groups form via intermediate peroxides.[5] In vacuum (step 2), if a methyl (or other branch) is adjacent to the radical site, then the formation of *trans* unsaturation may be accomplished by the evolution of the methyl (or branch) radical. That is, the unsaturation results from the successive evolution of H· and then the adjacent R· to form *trans* unsaturation. Thus, both the formation of *trans* unsaturation and methyl decay seen in the infrared spectra of the vacuum-irradiated

sample are accounted for. In the presence of oxygen (i.e., air), however, the initial radical formed by C—H scission may be attacked by oxygen (as shown in step 3) with the formation of a highly reactive peroxy radical,
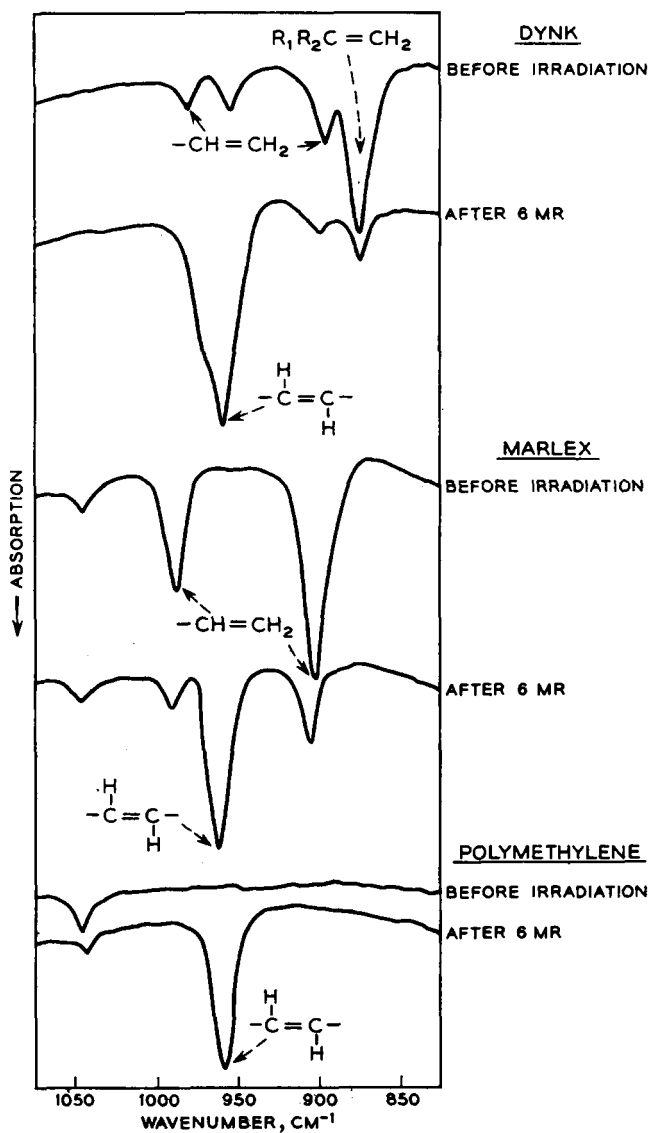

Fig. 3. Unsaturation region of three polyethylenes before and after irradiation at 6 MR.

thus preventing stabilization by the expulsion of the alkyl groups. Therefore in air, methyl decay is suppressed.

From the relative intensities of the *trans* group bands it was noted that the amount of *trans* groups formed in the presence of oxygen (i.e., air)

was less than in vacuum. This is also believed due to the competitive formation of peroxides.

Another mechanism leading to the formation of *trans* unsaturation was suggested by Miller et al.[6] In this reaction, C—H fracture may cause simultaneous expulsion of an adjacent hydrogen atom with the evolution of molecular hydrogen (H_2). Analogously, this mechanism produces $C_2H_4{}^+$, which is the major radical in the mass spectrum of ethane. The preference for *trans* formation was also considered by an examination of a molecular model of polyethylene. If two adjacent hydrogen atoms are removed, the formation of *trans* groups could be accomplished with only a slight rotation of the backbone, whereas *cis* formation would require a severe, almost 180° rotation.[6]

The appearance of the —OH and C═O bands at 3350 cm.$^{-1}$ and 1730 cm.$^{-1}$ and the background depression in the air-irradiated DYNK sample shows the formation of oxidation products which form as a result of oxygen attack on the radicals. With regards to the 720–730 cm.$^{-1}$ methylene rocking doublet, it is known that a major part of the 730 cm.$^{-1}$ component is sensitive to the crystallinity content in polyethylene samples. Consequently, the ratio of the absorbances at 730 and 720 cm.$^{-1}$ is often used to estimate relative crystallinity content in a series of polyethylene samples. The absence of the 730 cm.$^{-1}$ component in the vacuum-irradiated (500 MR) sample shows that a considerable amount of crystallinity has been destroyed by irradiation. In the air-irradiated (500 MR) sample, however, there is little or no effect on the crystallinity. The mechanism for this significant difference in the effect of irradiation on polyethylene crystallinity is not clear at the present time.

In Figure 3, we take a closer look at the unsaturation region of the spectra. The top two traces show this region for DYNK before and after 6 MR irradiation. The lower traces are those of Marlex before and after similar irradiation. In DYNK, before irradiation, most of the unsaturation is of the external vinylidene type. After a dose of 6 MR, *trans* unsaturation (at 964 cm.$^{-1}$) increases and the vinylidene (at 888 cm.$^{-1}$) decreases.

In Marlex, almost all the unsaturation is of the terminal vinyl type (CH═CH$_2$) as shown by the bands at 990 and 910 cm.$^{-1}$ Here again, after only a 6 MR dose, the *trans* groups form rapidly, and the vinyl groups at 990 and 910 cm.$^{-1}$ decrease. Because of the rapid increase of *trans* groups during irradiation and the simultaneous decrease of the other unsaturated groups, it might appear that the *trans* groups are being formed from a reaction involving the sacrifice of the other unsaturated groups in the polymer. In order to determine the validity of this observation, a sample of polymethylene which has no infrared-detectable unsaturation or branching was exposed to similar doses of irradiation. In Figure 3 (lower curves) we see that in polymethylene, the *trans* unsaturation band still forms strongly after irradiation in either air or vacuum. This means that the *trans* groups come from a reaction that is independent of either un-

saturation or branching. As for the vinyl and vinylidene decay, although there is no conclusive mechanism to explain their disappearance, they probably become saturated by atomic hydrogen in the system or become crosslinking sites.

B. Single Crystals

Single crystals of Marlex collected as a cake by the slow-filtration technique and as a film by fast-filtration, as well as the bulk sample, were exposed to identical doses of radiation. Examination of the infrared spectra
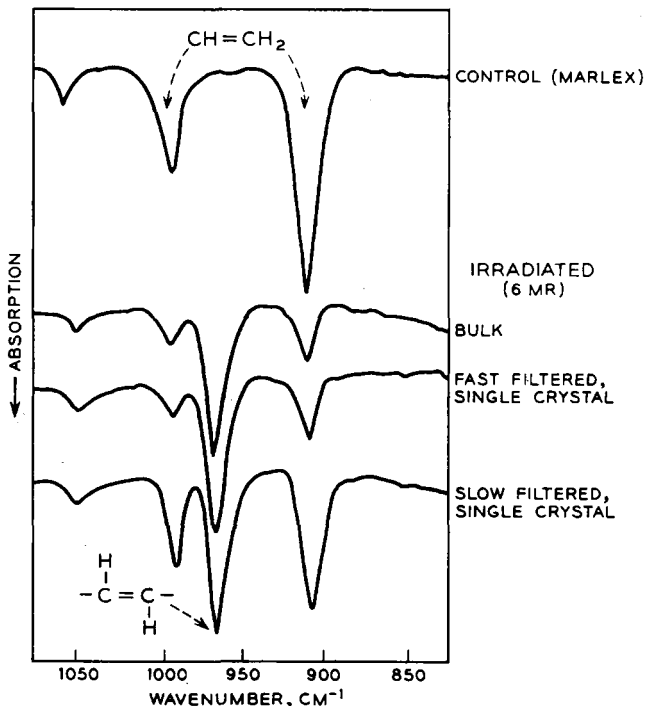

Fig. 4. Unsaturation region of single crystals of marlex before and after irradiation at 6 MR.

of these materials after irradiation (Fig. 4) shows that although vinyl groups decreased in all the samples after identical irradiation doses, vinyl decay in the bulk and fast-filtered samples was much greater than in the slow-filtered material. Consequently, all three Marlex specimens were irradiated at various doses and the intensities of the vinyl and *trans* groups were measured (by use of the 1370 cm.$^{-1}$ band as an internal standard) and plotted versus dosage. It can be seen in Figure 5 that vinyl groups in the bulk sample and the fast-filtered crystals decay rapidly at approximately the same rate. In the slow-filtered crystals, however, the rate of decay is considerably slower. In Figure 6, the formation of *trans* groups
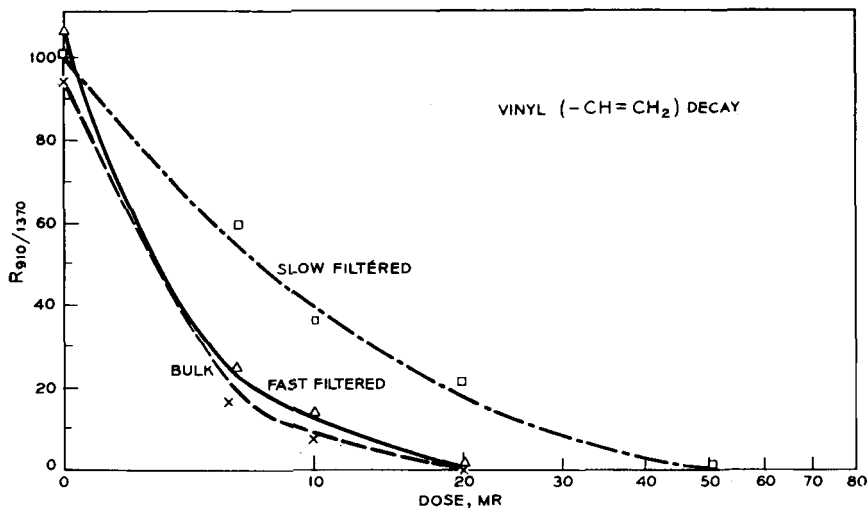
Fig. 5. Comparison of vinyl decay rate in single crystals and bulk as a function of irradiation dose.
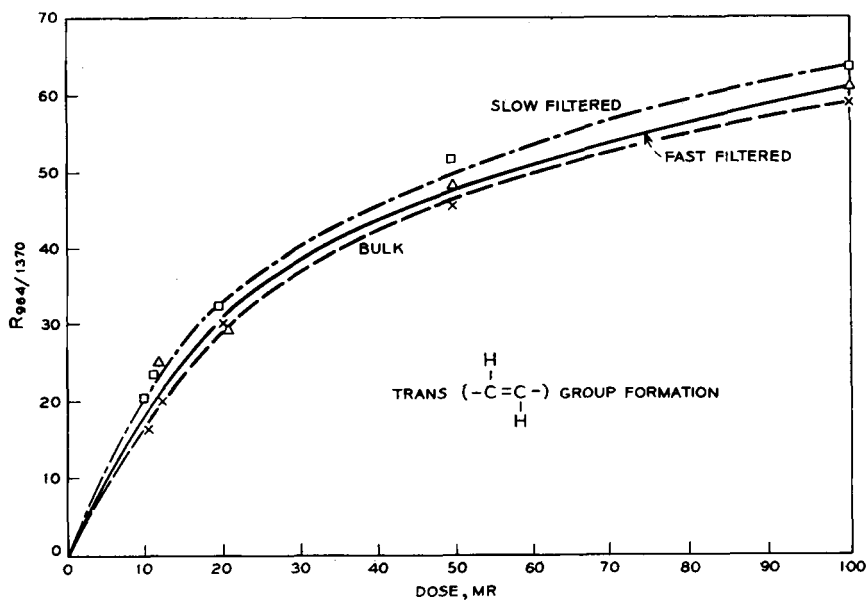

Fig. 6. Formation of *trans* unsaturation as a function of irradiation dose.

as a function of irradiation dose shows that the rate of *trans* formation is the same in all samples (indicating again, the formation of *trans* groups is independent of vinyl decay).

In the bulk and fast-filtered samples it has been observed that gel formation increases rapidly with dose while the gel formation in the slow-filtered

sample is considerably suppressed[4] (Fig. 7). Analysis by mass spectroscopy indicated that the slow-filtered sample still contained approximately 0.2% xylene, even though it had been dried in an oven. It is believed that trapped interlamellar xylene protects the ruptured C—H bonds, suppressing interlamellar crosslinking and gel formation.
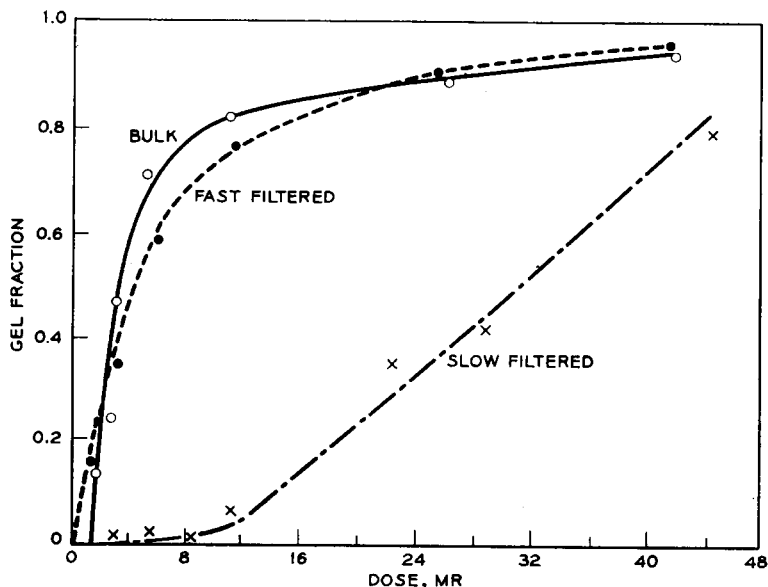

Fig. 7. Comparison of gel formation in single crystals and bulk polyethylene as a function of irradiation dose.

The low rate of vinyl decay and the suppressed gel formation in the irradiated slow-filtered single crystals may be related. Accordingly, since the vinyl groups are terminal groups and therefore somewhat mobile, it is possible that many of them are excluded from the crystal lattice of the solution crystallized material and occupy interlamellar sites (Fig. 8). In that case, the vinyl groups would be in contact with trapped interlamellar xylene which would similarly protect them. This 'protection effect of xylene will be discussed below. As for the internal *trans* groups, they are probably formed at random along and in the folded molecular chains of the crystal lattice and are unaffected by traces of xylene between lamellae.

The protection effect of xylene, and aromatic structures in general, may be seen by examining the spectra of polystyrene before and after irradiation in air and vacuum (Fig. 9). The only significant change in the spectra after irradiation in air is the slight increase of the carbonyl band 1730 cm.$^{-1}$ in the air-irradiated sample. The high resistance of the aromatic structure of polystyrene is evidenced by the fact that the yield of hydrogen (the major decomposition product of hydrocarbons) is considerably lower in simple aromatic compounds than in aliphatics.[8] In addition, Manion and Burton[7]

found that in the irradiation of a mixture of benzene and cyclohexane, the benzene actually protected the radiation-sensitive cyclohexane while the benzene was relatively unaffected by the irradiation.

These experiments show that not only is the aromatic ring extremely stable to irradiation but that it can also exert protection on nearby radiation-sensitive groups. This stability and protective effect of the benzene ring during irradiation is believed due to the absorption of radiation energy
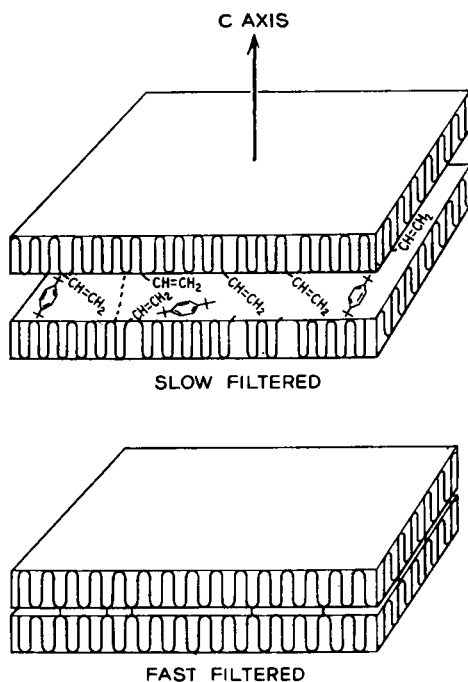

Fig. 8. Xylene protection of vinyl groups and cross-linking sites in single crystals of polyethylene.

and its dissipation in the resonance of the aromatic ring. Therefore, it is possible that the presence of xylene trapped between the lamellae of the slow-filtered single crystals suppresses both the crosslinking and the vinyl decay.

In an attempt to examine the presence and the protective effect of inter-lamellar xylene, the slow-filtered single crystals (prepared from dilute xylene solution) were washed several times with acetone, dried in a vacuum oven at 40°C. and then under high vacuum (10^{-6} mm. Hg) for 16 hr. It was hoped that by either removing or replacing trapped interlamellar xylene with acetone, the rate of vinyl decay in the slow-filtered single crystals would be similar to that in the bulk or fast-filtered samples. However, after irradiation of the acetone-washed slow-filtered crystals, the infrared spectra showed that the low rate of vinyl decay was essentially unchanged.

Subsequent analysis of the acetone-washed crystals by mass spectroscopy showed that the xylene had, in fact, not been removed by the acetone and is apparently tenaciously trapped in the slow-filtered single crystals.

However, it was found possible to remove most of the trapped xylene by melting the slow-filtered preparation before irradiation. Vinyl decay in
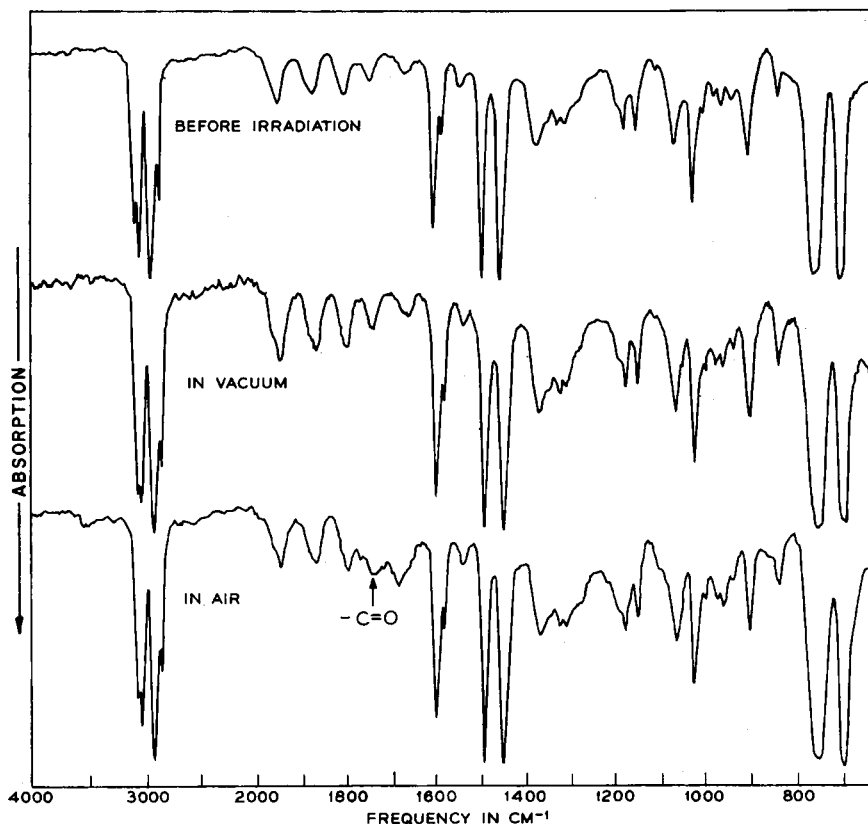

Fig. 9. The effect of irradiation (500 MR) in air and in vacuum on polystyrene.

this (premelted) preparation then corresponded to that in the bulk and fast-filtered samples.

Therefore, the continued low rate of vinyl decay in the slow-filtered single crystals, after irradiation, is probably due to the presence of trapped interlamellar xylene.

SUMMARY

The infrared spectra of irradiated bulk and single crystals of polyethylene show some of the structural rearrangements that occur on irradiation in air or vacuum.

In addition to the radiation-induced decay of vinyl and vinylidene groups, there is a simultaneous and rapid increase in *trans* unsaturation independent of either other unsaturated groups or branching.

The influence of oxygen during irradiation was noted. Irradiation of a branched polyethylene in vacuum produced a decrease in the methyl content as well as a decrease in crystallinity. In air, however, there was little or no decrease in either methyl content or crystallinity.

Infrared spectra of irradiated single crystals of polyethylene prepared by two different methods showed that the rate of vinyl decay during irradiation was dependent on the manner in which the single crystals were prepared. From this observation, the location of the vinyl and *trans* unsaturated groups in the single crystals are indicated. The protective effect of aromatic structures to irradiation was also noted.

From these data, certain reaction mechanisms are postulated.

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Synopsis

The irradiation of polyethylene causes a number of molecular rearrangements in the chemical structure of polyethylene. In addition to the significant changes in the type and distribution of unsaturated groups, an infrared comparison of the radiation induced chemical changes that occur in air and in a vacuum showed that the presence of oxygen has a marked influence on the structural rearrangements that occur on irradiation. The infrared spectra of irradiated single crystals prepared by two different means indicated the location of vinyl groups in the crystals and their protection from radiation by aromatic structures. From these data, a number of reaction mechanisms are postulated which can contribute to our understanding of irradiation effects on polyethylene.

Résumé

L'irradiation du polyéthylène provoque un certain nombre de réarrangements moléculaires dans la structure chimique du polyéthylène. En plus des changements importants dans le type et la distribution des groupes insaturés, une comparaison effectuée par analyse infra-rouge sur les changements chimiques induits par la radiation, tant à l'air que dans le vide, montre que la présence d'oxygène a une influence marquée sur les réarrangements structuraux qui ont lieu par irradiation. Les spectres infra-rouges effectués sur des cristaux uniques irradiés, préparés par deux voies différentes, montrent la position des groupes vinyliques dans les cristaux ainsi que la protection qui leur est offerte vis-à-vis de la radiation par les structures aromatiques. À partir de ces résultats on a pu pro-

poser un certain nombre de mécanismes de réaction qui peuvent contribuer à notre compréhension des effects de l'irradiation sur le polyéthylène.

Zusammenfassung

Die Bestrahlung von Polyäthylen führt zu einer Reihe von Molekülumlagerungen in der chemischen Struktur von Polyäthylen. Zusätzlich zu den charakteristischen Veränderungen des Typs und der Verteilung ungesättigter Gruppen zeigte eine Infrarotuntersuchung der strahlungsinduzierten, unter Luft und im Vakuum auftretenden Veränderungen, dass die Gegenwart von Sauerstoff einen ausgeprägten Einfluss auf die strukturellen Umwandlungen bei der Bestrahlung hat. Die Infrarotspektren von bestrahlten, nach zwei verschiedenen Verfahren hergestellten Einkristallen liessen das Vorhandensein von Vinylgruppen in den Kristallen und ihren Schutz gegen Strahlung durch aromatische Strukturen erkennen. Auf Grund der Ergebnisse werden eine Reihe von Reaktionsmechanismen aufgestellt, die einen Beitrag zum Verständnis der Bestrahlungseinflüsse auf Polyäthylen liefern.