Radiation Effects in Polyethylene Films Studied by Pulse Radiolysis

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Summary Pulse radiolysis of polyethylene film produces an optical absorption band attributed to the trapped electron and, with aromatic compounds as scavengers, results in the formation of ions and excited states from these additives; the technique is applicable to films of other translucent materials.

Radiation-induced processes in thin films of polyethylene, with an optical path length of about 0·1 mm, can readily be studied by pulse radiolysis, employing the very high radiation dose delivered to such a film by a 600 kV Febetron (Field Emission Corporation, Model 706). The polyethylene film (I.C.I., Q1288 additive free) was held at an angle of 45° to both the electron beam and the analysing light in an evacuated cell. The dose from a single pulse (5 ns) was *ca.* 5×10^{18} eV g^{-1}.

Pulse radiolysis of polyethylene produced a long-lived absorption band in the region below 320 nm, increasing in intensity with decreasing temperature, which is attributable to free radical and unsaturated species previously observed in γ-ray studies.[1] At 95 K, an absorption band was observed with the band maximum apparently above 1050 nm; this band was not present at room temperature. Unlike absorption bands attributable to molecular ions, this long wavelength band decayed significantly on the microsecond time scale at 95 K. In view of this and on the basis of comparison with similar bands in alkane glasses and liquids,[2,3] and the decrease in the absorbance with electron scavengers [CCl_4 and $C(NO_3)_4$] but not with hole scavengers (di- and tri-ethylamine) present, the band is attributed to trapped electrons.

At 298 K, polyethylene with dissolved naphthalene (10^{-3}—10^{-1} mol l^{-1}) or pyrene (5×10^{-4}—5×10^{-2} mol l^{-1}), showed transient absorption bands attributed to the following species (absorption maxima/nm in parentheses): naphthalene radical anion (325, 298), naphthalene first excited triplet (416, 393, 390), pyrene radical anion (494), pyrene radical cation (454), and pyrene first excited triplet (414). Emission was observed from naphthalene and pyrene singlet excited states, pyrene excimer, and bipyrenyl. The absorbance due to the ionic species attained a maximum within the rise-time of the apparatus (*ca* 20 ns). The absorbance increased with increasing additive concentration, towards a limiting maximum absorbance at the highest concentration used, for all of these species except for the pyrene cation. The latter attained a maximum value at a pyrene concentration of about 10^{-2} mol l^{-1} and decreased at higher concentrations. The anion bands were decreased competitively by electron scavengers, the cation bands by positive-hole scavengers, and the triplet-state bands by both types of scavenger. The anion absorbance decayed by second-order kinetics, the rate for naphthalene being about 100 times that for pyrene. The pyrene cation decayed at a rate similar to that of the pyrene anion but, in this case, not by simple second order kinetics. Growth of the triplet absorption during the ion decay was not observed.

No evidence has been obtained in the pulse radiolysis experiments to support the suggestion[4] that migratory excitation plays a major part in the formation of ions from aromatic solutes in irradiated polyethylene. The main results of the present work can be interpreted in terms of primary radiation absorption by the polymer to give positive holes and electrons, which migrate rapidly and which can be scavenged by an aromatic additive in competition with recombination and trapping processes. Excited states of the aromatic additives appear to be produced mainly by aromatic cation–electron recombination. The scavenging efficiency of additives at low concentrations and the rapid formation of ions and excited states from the additives indicate rate constants for charge scavenging and recombination comparable with those reported for some organic liquid systems.[3]

The pulse radiolysis technique used for polyethylene films is suitable for application to thin films of other materials, including gels and membranes of biological significance.

We thank the S.R.C. for financial support and I.C.I. Ltd. for the polyethylene samples.

(*Received*, 6*th May* 1974; *Com.* 518.)

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