The principal results are summarized in Figure 1. If one adopts eq. (1), the range in p_{11} appears to be about 5.16×10^4 dynes/cm.^{2} to 10^6 dynes/cm.^{2}, whereas eq. (2) predicts a range of about 29.3 dynes/cm.^{2} to 1.84×10^5 dynes/cm.^{2}. Qualitatively, at least, both methods should yield the same description of elastic effects in shear. Obviously, further experimental intercomparisons of this kind are needed to establish that method which yields the more realistic measure of normal stresses. It is hoped that these observations will stimulate others to obtain more detailed intercomparisons of these methods with the use of a variety of viscoelastic materials.

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Radiation-Induced Crosslinking of Polymers and Polymerization of Paraffinic Hydrocarbons

Damage in polymers and other organic solids caused by ionizing radiation is currently receiving much attention, not least because the problem of "radiation protection" requires solution in many practical applications. Ideally, a study of "protection" should be preceded by an understanding of the mechanisms by which these radiation-induced chemical changes take place. This applies particularly also to the topic of radiation-induced crosslinking in such polymers as polyethylene and related solid paraffinic hydrocarbons.

Lawton et al.[1] have interpreted the results of electron spin resonance studies of irradiated polyethylene as lending support to a mechanism of hydrogen atom abstraction. On this hypothesis, free radicals are supposed to be formed in pairs on neighbouring molecules and to combine to form a crosslink. Migration of the free radicals plays no part in this theory. However, similar experiments on polyethylene by Charlesby et al.[2] have been interpreted in terms of migrating free radicals which form crosslinks when they meet. It is therefore necessary first of all to examine briefly the experimental data from which these deductions were made.

The major part of these two papers consists of a study of the decay of electron spin resonance amplitude at room temperature subsequent to irradiation at liquid nitrogen temperature. Concerning the shape of the decay curve,

the two papers are in apparent disagreement. Lawton et al.[1] find it to be exponential, while Charlesby et al.[2] state that it is hyperbolic, corresponding to second-order kinetics. A closer perusal of the published curves reveals that the time scales over which the decay has been measured are rather different in the two cases, and that the actual decay shows approximately hyperbolic and exponential forms successively. It seems, therefore, that analysis of the results in terms of either monomolecular or bimolecular recombination is not satisfactory.

Interpretation of the E.S.R. experiments involves two assumptions. The first is that the six-line spectrum is that of the $(-CH_2 \cdot CH \cdot CH_2-)$ free radical. The second, of a more doubtful nature, is that the disappearance of these free radicals is directly related to the formation of crosslinks. However, no proof exists to show that these two events are connected with one another.

There are certain experimental results on crosslinking which any competent theory must be able to explain unless future work should prove these results to be incorrect, viz., (1) the extremely small temperature dependence[3] of the crosslinking efficiency between -196 and $100°C.$, and (2) the protection against crosslinking[4] afforded by small concentrations of suitable "impurities."

Neither of the theories is capable of explaining both these facts. The Lawton hypothesis cannot account for the protection effect, as the effective concentrations of impurities are so low that a given impurity center would be on the average too far away from a (hypothetical) radical pair to be effective, and the diffusion coefficients of impurities must be very small.

The Charlesby mechanism cannot account for the experimental facts given under (1), as free-radical migration (which at best is effectively hydrogen atom migration) would have a significant activation energy of not less than 0.3 e.v. The curve given by Charlesby and Davison[3] shows two activation energies, the larger of which works out at approximately 0.004 e.v. They found in the yields an increase by a factor of 4, from $-100°C.$ to $+100°C.$, whereas assuming an activation energy of 0.3 e.v. one would get an increase by a factor of 5×10^4.

Unfortunately, we do not, in fact, possess any information about the temperature dependence of the actual yield of crosslinking at low temperatures because the data referred to above correspond to measurements of crosslinking at ambient temperature and nothing is known about how much and at which temperature the actual crosslinking takes place during the "warming-up period[7]" e.g., in going from liquid nitrogen towards room temperature. It would clearly be essential to use a method by which the crosslinking can be assessed at the temperature at which the irradiations are carried out.

One must conclude, therefore, that the above suggestions do not provide an adequate basis for a crosslinking mechanism unless the experimental findings are shown to be considerably in error. It may well be that the processes described by these authors occur in irradiated polyethylene but their relevance to the phenomenon of crosslinking has not been established.

Dependence of the crosslinking on dose rate could give some very valuable information on the mechanism of this process. There are, however, no published figures available except a short reference[3] to certain yields of crosslinking
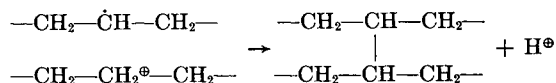
which showed no significant changes in a dose rate range of 10^2–10^6 rad/sec. Detailed and quantitative experiments are needed to settle this point.

It has been suggested[5,6] that electronic processes are of considerable importance in the radiation-induced reactions in solids, in general, and also, in particular, for the crosslinking in paraffinic hydrocarbons; the formation of *trans* vinylene groups and the effect of molecular oxygen can also be explained from this point of view. Conductivity experiments have shown[7] that dissolved oxygen molecules can act as electron traps, and this may lead to the formation of peroxidic compounds. In general, crosslinking can be expected to occur only when two carbon atoms of different chains are in sufficiently close proximity, of the order of 1.54 A. It can be easily shown that even with the most densely ionizing radiations the probability that an appreciable number of free radicals is created primarily on two closely adjacent carbon atoms must be extremely low; the question, therefore, arises as to how, in view of these circumstances, such crosslinks can be formed with a relatively high probability. A "collision" mechanism leading to an ionic mechanism for crosslinking is provided by the fact that these solid hydrocarbons exhibit radiation-induced electrical conductivity which, in long-chain paraffinic hydrocarbons, has a component due to free holes.[7] Such a mechanism would be capable of accommodating the findings under (1) and (2).

Mass spectroscopic data can provide a very useful guide for the consideration of ionic reactions. In the condensed state, however, the "solvation" energies of the initial and the resulting ions must be taken into account; the solvation energy of a relatively small ion in the solid (e.g., H_2^+), as estimated, for example, by Born's formula, may be appreciable, even in a medium with a relatively low (optical) dielectric constant.[2] Moreover, the ions produced by ionizing radiations would, in general, not be in their ground states and might undergo reactions to a greater or lesser extent before they will have lost an appreciable part of their excitation energy.

Several ion–molecule reactions have been suggested[5,6] to account for the reactions in the irradiated hydrocarbon polymer. Recent work has led to the conclusion that the crosslinking reaction may be an interaction between a free radical and an ion according to:

$$-CH_2-\overset{\cdot}{C}H-CH_2- \qquad -CH_2-CH-CH_2- $$
$$\rightarrow \qquad\qquad | \qquad\qquad + H^{\oplus}$$
$$-CH_2-CH_2^{\oplus}-CH_2- \qquad -CH_2-CH-CH_2- $$

That is, a radiation-produced (frozen-in) radical interacts with a *mobile* hole as shown above, or it may give a hydrogen atom with subsequent neutralization of the positive charge on the polymer.

In a recent very informative paper Libby[8] has dealt in some detail with the chemistry of positive hydrocarbon ions in general, and their role in the radiation-induced crosslinking of paraffinic hydrocarbons. In his paper there is also a fuller discussion of the possible role of hydrogen abstraction by hydrogen atoms in the mechanism of crosslinking, and it is concluded that such a mechanism is very unlikely to occur.

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POLYMER NEWS

The Society of the Plastics Industry, Inc.

Calender of Coming Events

February 5–7, 1963: 18th Reinforced Plastics Division Conference, Edgewater Beach Hotel, Chicago, Illinois.

April 24–26, 1963: Cellular Plastics Technical Conference and Division Meeting, The New York Hilton Hotel, New York City.

April 29, 30, 1963: 21st Annual SPI Canadian Section Conference, Chateau Laurier Hotel, Ottawa, Canada.

May 8–10, 1963: 20th Annual SPI Western Section Conference, Rivera Hotel, Palm Springs, California.

June 13, 14, 1963: 5th Annual Plastics for Tooling Seminar, Purdue University, Lafayette, Indiana.

November 18–22, 1963: 10th SPI National Plastics Exposition, McCormick Place, Chicago, Illinois, and SPI National Plastics Conference, Sheraton-Chicago Hotel, Chicago, Illinois.

February 4–6, 1964: 19th Reinforced Plastics Division Conference, Edgewater Beach Hotel, Chicago, Illinois.