Response to commentary by M. Dole

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In his commentary M, Dole raises four points concerning the results of our paper which he states are at variance with previous work. We would like to comment on each of the points and their implications on the paper in question.

We reported observation of approximately an order of magnitude difference in the number of free radicals observed by e.s.r. and the number of chemical changes detected by i.r. M. Dole states that there should be a much better agreement between these two numbers. Such agreement would be more in line with what we expected for mechanical damage and, as stated in the original paper, the radiation studies were primarily conducted to help lay a basis for the mechanical studies. We reported, however, only what we observed in what we considered to be carefully conducted experiments. Re-evaluation of our paper in light of M. Dole's comments still leads us to conclude that for our studies i.r. indicates more chemical damage events than does e.s.r. This is qualitatively analogous to, but much lower in magnitude than, that reported for mechanical damage by Zhurkov *et al.*[1].

1. Free radical yield

Based on the order of magnitude difference between the G value calculated from our data and previous determinations M. Dole raises questions concerning saturation of our e.s.r. measurements and calibration of the γ source used in our work. The major emphasis in our previous work has been concerned with mechanically induced radicals. For this reason our saturation experiments had been carried out on polymer specimens damaged by mechanical means.

Saturation might be defined in various ways. It is sometimes defined as the first indication of nonlinearity in a plot of signal amplitude *versus* square root of power level. By this definition most polymer free radicals as well as the 'pitch standard' begin to show some signs of saturation at microwave power levels approaching zero. We feel that always restricting e.s.r. studies to power levels below this point might be overly prohibitive.

In Figure 1 we have plotted e.s.r. signal intensity *versus* microwave power level both for the 'Varian* standard pitch' reference and ground polyethylene. It will be noted that neither of these materials exhibits a linear response over any part of the power range in which our E-3 instrument operates (>0.25 mw). They do, however, exhibit very similar signal intensity *versus* power. The quantitative measure of the free radical intensity obtained by double integration of the polymer spectra and comparison with the Varian reference at the same power level is shown as the upper (horizontal) curve in *Figure 1*. This can be interpreted as indicating that the apparent unpaired spin concentration is very nearly independent of power level from 1/4 to several milliwatts power level. These results were obtained at a 100 kilohertz modulation amplitude of 10 Gauss. Very similar results were obtained at modulations of 1 and 0.5 Gauss but with substantially reduced signal strength and hence slightly more scatter. We and others have obtained results similar to those in *Figure 1* for mechanically degraded nylon and other polymers.

Based on our experience with mechanically degraded polymer specimens a power level near one mw was chosen as a reasonable compromise between a level at which spectra could reasonably be obtained and one at which saturation effects dominate. In the paper by Gvozdic and Dole[2], which was published after our paper was in press, it was pointed out that deviations from linearity occurred at power levels of 0.063 mw for γ-irradiated polyethylene. The discrepancy in saturation power may reflect differences in the means of producing radicals as well as the definition of saturation.

We have now run saturation experiments on γ-irradiated polyethylene and find, as shown in *Figure 2*, that the onset of saturation occurs at lower power levels

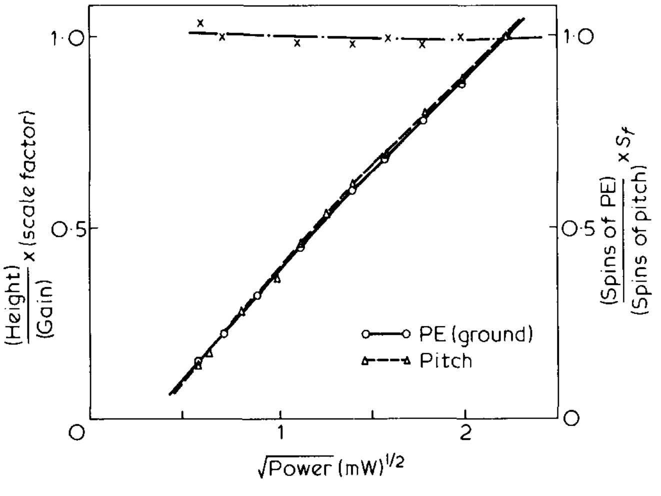

Figure 1 The sloping curves compares e.s.r. signal height for ground polyethylene with that of the Varian reference as a function of microwave power level. They have been scaled to give the same initial slope. Numerical double integration of both spectra demonstrated that the signal height is proportional to the area under the absorption curve. The upper nearly horizontal curve (marked by x——x) is the calculated number of unpair spins for the polyethylene *versus* power level determined by computer comparison with the pitch at the same power level. Note the curves do not extrapolate through zero, this can probably be attributed to a small (−0.09 mw) error in the setting of the power dial. This offset has been the same over the years for all samples we have tested

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* Certain commercial materials and equipment are identified in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply necessarily the best available for the purpose.

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than for mechanically induced radicals. We cannot, at this time, explain the difference in the saturation behaviour of radicals produced by different methods. We observed one other rather surprising result. It was found that there was a marked difference in the saturation behaviour of radicals produced, continuously maintained, and measured by e.s.r. at near cryogenic temperatures and those which had experienced an intermittent warming before recooling and recording e.s.r. spectra at cryogenic temperatures. *Figure 2* shows the e.s.r. spectrum intensity as a function of power level for a sample where the sample tube was exposed to room temperature conditions for two minutes. The intensity scale for this sample is a factor of 5 lower than that for the other specimen. Not only is the signal significantly weaker but it shows signs of saturation at lower power levels. Samples held at room temperature for 30 min exhibited almost complete saturation at 1/2 milliwatt. That is, the e.s.r. spectra intensity increased only slightly with power from 1/2 to 5 mw. We were not aware of this at the time we made our measurements but it does not appear to significantly affect our results or conclusions.

We estimate the saturation effect on the *G*-values determined from our data to be no more than 30%. The error due to variability in the filling factor between our samples and the 'pitch' standard was included in our original data analysis.

M. Dole also inquired about the calibration of the γ-source used. The Cs source used in our studies is maintained by the faculty and staff of the Radiological Biology Department of the University of Utah to whom we are indebted for use of the source and information relative to its calibration. This source (a Cs G-B-150 irradiator) had been calibrated prior to exposure of our specimens using standards traceable to the National Bureau of Standards. The source calibration is also periodically checked with a Victoreen Instruments Co. Model 570 R-meter by Radiological Biology Department staff.

As pointed out by Gvodic and Dole[2] the positioning of the specimens within the radiation chamber can affect exposure. The doses given in our paper were calculated for the sample centre. We would estimate that this dosage should vary by no more than 30% over the sample length. We estimated the positioning effect to lead to an error of no more than 20% in the dose levels. Combining errors from all sources the *G* value determined from our data could be as much as a factor of two larger but not in the range suggested by M. Dole. Thus, we agree with M. Dole that the exact cause of the discrepancy in *G* values is unknown.

2. Double bond yields

As pointed out by M. Dole our value of *G* for *trans*-vinylene formation at 3 Mrad exposure is within 10% of his value. In generating his value of 0.31 for the ratio of *trans*-vinylene produced to free radicals M. Dole divided his *G* value for *trans*-vinylene by his *G* value for free radicals, i.e., 1.03/3.3. We used a similar procedure to arrive at our value; the discrepancy in the ratio arises almost entirely from differences in the *G* value for free radicals.

3. Crosslink yields

The statement concerning crosslink yields in our paper is referenced from the literature, including a book by M. Dole[3], that can be referred to for a more complete discussion. As stated in our paper, we did not make any crosslinking measurements. Rather, we gave a composite value of $G(x)$ for PE irradiated at several different dosages and temperatures based on the work of several others (including the text by M. Dole).

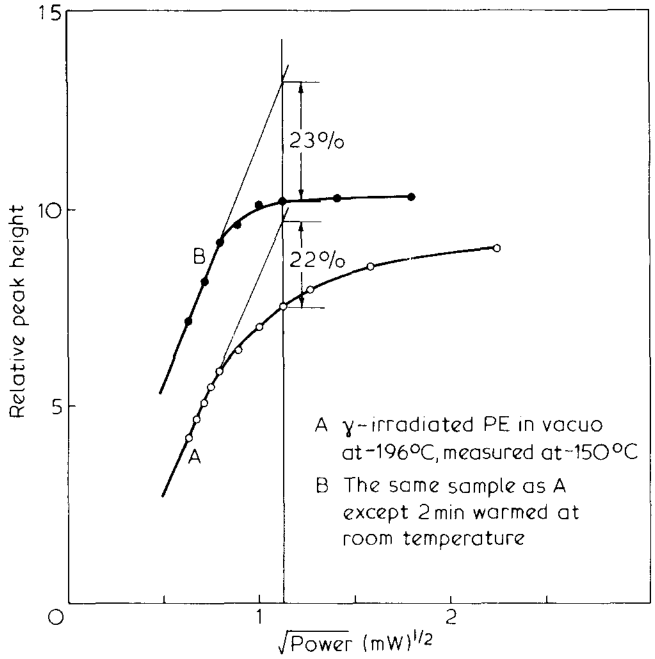

Figure 2 Signal height *versus* microwave power level for polyethylene samples that have been irradiated (Cs-137 source for about 3 Mrads) in vacuum at liquid nitrogen temperature. Spectra were recorded at –150°C under the following conditions: open circles, immediately after γ-irradiation, and closed circles, after exposing the sample tube to room temperature for two minutes before again cooling to 150° C for taking of subsequent spectra. The intensity scale of the specimen held at room temperature is less than 20% of that of the original sample. Samples irradiated in air exhibited very similar power saturation behaviour. The curves may not extrapolate to zero for the reason given in the caption of *Figure 1*

The point we were trying to make was that a $G(X)/G(t\text{-VI})$ value of approximately 1 did not significantly affect our conclusions. While M. Dole is, in all likelihood, correct that this ratio varies from 0.4 to 1.6, this again does not affect our conclusions. Particularly in light of the other uncertainties in comparing e.s.r. and i.r. results on small signals it does not appear worthwhile to try to be too precise in determining $G(X)$.

Carbonyl group formation

M. Dole has apparently not read our paper carefully concerning this point. We were surprised to find carbonyl groups forming in an evacuated system and attributed them to trapped oxygen rather than subsequent exposure to atmospheric oxygen. For the following reasons we still believe this to be the case: (a) M. Dole notes that 'The allyl free radicals are so stable at room temperature that they will react with air to form carbonyl groups for as long as two months after irradiation'. While we do not disagree with this statement, some other observations are in order, that shed some light on the extent of this effect. When our irradiated specimens were brought to room temperature in a vacuum and held at this temperature for approximately 10 min before recooling to –150°C, most of the radicals had disappeared. Using the saturation power level of 0.063 mw given by M. Dole it appears that the residual signals after warming for a few minutes is reduced at least by an order of magnitude from the original spectra produced by irradiation at liquid nitrogen temperature. (b) Most of our samples were kept sealed for several days to weeks prior to opening the sealed tubes. A few, however, were opened within one day of warming. Infra-red measurements indicated no detectable differences with time of exposure to atmospheric oxygen subsequent to warming for periods ranging from one day to approximately a year. Thus, it is less likely that the major source of oxygen for carbonyl formation was exposure to air subsequent to γ-irradiation than that it was due to trapped oxygen.

In conclusion, we have re-examined our data in light of the comments by M. Dole and are unable to explain fully the discrepancies. Possible causes may be attributable to differences in measuring techniques, nature of the radiation source or other causes which cannot be assumed at this time.

References

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2 Gvozdic, N. and Dole, M. *Radiat. Phys. Chem.* 1980, **15**, 435

3 Dole, M. 'Radiation Chemistry of Macromolecules', Academic Press, 1972

E.p.r. studies of the thermal polymerization of phenylacetylene

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Interest in the polymerization of acetylenes has been sparked by the growing realization that polyacetylenes have semiconducting properties[1-4] and will probably find commercial application in the electronic industry.

The polymerization of acetylenes has been studied mainly with systems that involve transition metal coordination catalysts[5-18]. Coordination mechanisms are not well understood in all instances, and Ziegler–Natta processes are complicated because of the presence of metal alkyl co-catalysts.

For the polymerization of acetylenes by transition metal complexes alone, metals of group VIIB and VIII involve a metal-acetylide[5,8,10,14,16] as the initiator of the polymerization. Only terminal acetylenes are polymerizable by this method. Catalysts based on group VIB promote the polymerization of acetylenes by a series of 2+2 cyclo-additions.[12] Both terminal and internal acetylenes can polymerize by this process.

The purpose of the present study is to obtain information and insight into the mechanism by which phenylacetylene polymerizes thermally. In this communication we report the first electron paramagnetic resonance (e.p.r.) studies of the thermally produced radicals in phenylacetylene either *in situ* or by spin trapping techniques.

We have thermally polymerized phenylacetylene in the absence of air at 130°C for 2 h in an oven and observed the characteristic $\simeq 10$ Gauss peak-to-peak e.p.r. line width. This line is found to consist of more than 30 hyperfine components that are partly resolved and uniformly spaced about one Gauss apart. However, when the thermal polymerization of phenylacetylene was followed by placing the sample tube inside the e.p.r. cavity with a variable temperature insert, the e.p.r. spectrum initially observed at about 95°C is analogous to that of 1,4-diphenylbutadiene radical anion[19]. The spectrum is composed of at least four multiplets of hyperfine lines. Its major feature can be computer simulated by assigning $A_H = 3.75$ G (5 H) and $A_H = 0.85$ G (5 H). Although the number of each type of proton is not known for certain, the number must be at least this large to account for the relative intensities in the experimental spectra. The e.p.r. spectrum of similarly treated phenyldeuteroacetylene is narrower indicating that some, but not all, of the larger hyperfine couplings are from non-aromatic hydrogen atoms that are replaced by deuterium atoms. The importance of the CH part of phenylacetylene in the polymerization process is indicated by the fact that no e.p.r. spectrum was observed when 1-phenyl-1-propyne was heated for short periods at 130°C in the e.p.r. cavity or for more than 24 h at 130°C in an oven.

Thermal polymerization of phenylacetylene monomer in the presence of 2-methyl-2-nitrosopropane produces two spin adducts: di-t-butylnitroxide (DTBN) side product with a characteristic nitrogen hyperfine coupling of 15.60 G and a second nitroxide (I) ($A_N = 14.95$ G) having a doublet hyperfine coupling from a β-proton ($A_H = 3.18$ G).

Spin trapping of phenyldeuteroacetylene produces three spin adducts: the first two species are the same as the two spin adducts observed in the spin trapping of phenylacetylene with 2-methyl-2-nitrosopropane mentioned earlier except the doublet disappears while the deuterium broadens the nitroxide lines by unresolved hyperfine coupling. This latter species (II) has $A_N = 13.65$ G, a broader peak-to-peak width of about 1.5 G from which we estimate $A_D = 0.60$ G. All three species have close to identical g-values of about 2.0050. The third spin

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