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.

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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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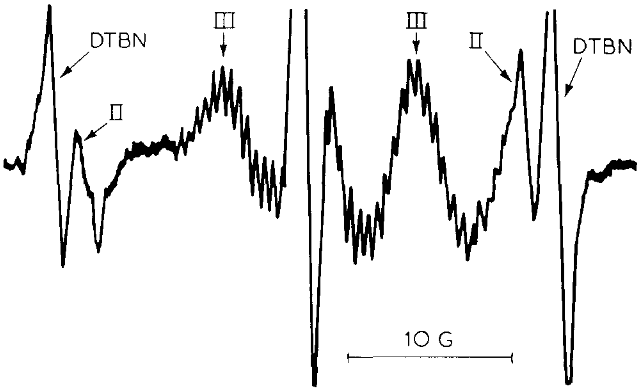


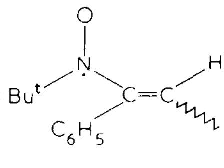
Figure 1 E.p.r. of transient species observed in the spin trapping at $C_6H_5C{\equiv}CD$

adduct (III) produced while initially heating phenyldeuteroacetylene and 2-methyl-2-nitrosopropane results in a complex e.p.r. spectrum shown in *Figure 1*. This e.p.r. spectrum features a triplet of multiplets with at least 12 hyperfine components in each multiplet. This spectrum can be simulated with $A_N = 5.85$ G (1 N), $A_H = 1.50$ G (3 H), $A_H = 0.50$ G (2 H), and $A_D = 0.50$ G (1 D).

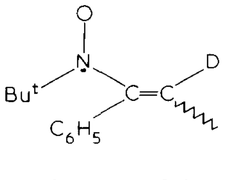
Several generalizations seem plausible, based on these results of e.p.r. studies of thermal polymerization of phenylacetylene. The small e.p.r. coupling constants indicate π-electron radicals. The large number of lines suggest that the unpaired electron interacts with more than one phenyl ring and the g-value agrees with that of hydrocarbon π-electron radical in which the spin is delocalized over several aromatic rings. The failure of methylphenylacetylene to polymerize suggests that the CH or CD site of phenylacetylene of phenyldeuteroacetylene is an important reactive site, though the terminal hydrogen or deuterium remains intact. Additionally, the magnitude of the coupling constants necessary to simulate the e.p.r. spectra are similar to those reported for 1,4-diphenylbutadiene radical anion[19]. The narrower e.p.r. line width resulting from the thermal polymerization of phenyldeuteroacetylene indicate that some of the positions with large hyperfine coupling constants are from non-phenyl protons. *INDO* semi-empirical self-consistent field molecular orbital calculations[20] for 1,4-diphenylbutadienyl radical anion and 1,3-diphenylbutadienyl radical anion predict the former to agree with the experimentally observed hyperfine coupling constant while the latter to have quite large hyperfine couplings for a vinylic proton contrary to the experimental results observed[21].

INDO calculations made on a number of model nitroxides also support the small hyperfine doublet splitting that is observed with phenylacetylene and spin trap (and that disappears with phenyldeuteroacetylene) is due to hydrogen β to the nitroxide and is consistent with the structures of I and II:

I :

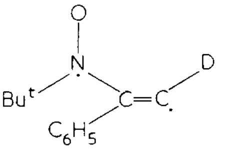


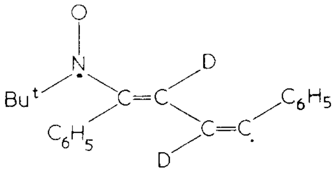
II :



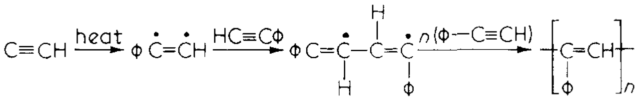
These results seem to imply that at the early stage of the polymerization process polymer growth begins as head-tail-tail-head. We have no further e.p.r. evidence to predict how the growing diradical will propagate. The complex e.p.r. spectrum shown in *Figure 1* might be an initial reactive fragment possibly a trapped monomer diradical $(\varphi\dot{C}=\dot{C}\text{–}H)$ or a short polymer diradical $(\varphi\text{–}\dot{C}=CH\text{–}CH=\dot{C}\text{–}\varphi)$ of the form:

III :





Based on these observations, a plausible reaction mechanism for the thermal polymerization of phenylacetylene might be initial formation of a phenylacetylene diradical followed by chain growth:



$$\Phi C{\equiv}CH \xrightarrow{heat} \Phi\dot{C}{=}\dot{C}H \xrightarrow{HC\equiv C\Phi} \Phi C{=}\underset{H}{\dot{C}}\text{—}\overset{H}{C}{=}\underset{\Phi}{\dot{C}} \xrightarrow{n(\Phi\text{—}C\equiv CH)} \left[\underset{\Phi}{C}{=}CH\right]_n$$

Fast electron exchange could account for the small nitrogen hyperfine coupling of approximately 6 G observed in *Figure 1*. We have not succeeded in detecting the e.p.r. absorption typical for radical pair formation at approximately half the field strength. This failure may, however, result from the low concentrations of species III that could be built up during the polymerization reaction.

It is not clear why 1-phenyl -1- propyne does not produce any e.p.r. signal when 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. We are currently in the process of investigating extensively the thermal polymerization mechanism of both terminal and internal acetylenes either *in situ* or by spin-trapping techniques.

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The dipole moment of poly-*p*-chlorostyrene

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Introduction

The dipole moment of a polar polymer is related to the orientation of the monomer units. The observed dipole moment is the statistical average of the molecular conformation. Since the mean-squared dipole moment of a chain in which the dipole moment is perpendicular to the main chain axis should not be affected by long range interaction, *i.e.* excluded volume effect[1], dielectric constant measurement is favorable for characterizing the molecular conformations.

In this communication, we report on the dipole moment of poly-*p*-chlorostyrene (PClSt) measured in cumene over a wide range of temperatures.

Experimental

The anionic polymerization of *p*-chlorostyrene was carried out in THF at −78°C under 10^{-6} mm Hg with Na-α-methylstyrene tetramer used as the initiator. The polymer obtained was dissolved in benzene, reprecipitated with methanol and dried in vacuum to a constant weight.

Determination of the intrinsic viscosity in cumene indicated its molecular weight which amounted to 6.7 × 10^4. Approximately the same value was obtained from the g.p.c. measurement of the molecular weight with toluene used as the eluent.

The dipole moment per monomer unit was determined by measuring the dielectric constant and the density of the cumene solutions of PClSt of several concentrations from 2 to 6% over a temperature range from 25° to 65°C. The cell was composed of coaxial platinum cylinders enclosed in a glass tube. The capacitance was measured by the heterodyne beat method at 500 kHz. Calibration of the apparatus was carried out by using purified benzene at each temperature measurement.

The specific polarization, p_2, of the polymer at infinite dilution was calculated according to the Halverstadt–Kumler equations[2].

$$p_2 = p_1\left(1 + \frac{3\alpha}{(\varepsilon_1 - 1)(\varepsilon_1 + 2)} - \frac{\beta}{d_1}\right),\; p_1 = \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}\cdot\frac{1}{d_1},$$

$$\alpha = \{(\varepsilon_{12} - \varepsilon_1)/w\}_{av} \text{ and } \beta = \{(d_{12} - d_1)/w\}_{av}$$

where, w is the weight fraction of polymer, ε is the dielectric constant and d is the density. The suffixes 1, 2 and 12 refer to solvent, solute and solution, respectively. The dipole moment per monomer unit, μ, was calculated by following equation;

$$\mu = \{9kT(P_2 - (MR)_D)/4\pi N\}^{1/2}$$

where, P_2 is the molecular polarization of a monomer unit in the polymer and is given by p_2 multiplied by the molecular weight of the monomer unit, $(MR)_D$ is the molecular refraction of the monomer unit, k is the Boltzmann constant, N is the Avogadro's number and T is the absolute temperature.

Results and Discussion

The experimental results are listed in *Table 1*. Cumene is a θ-solvent for PClSt (θ = 59.0°C)[3]. Our previous study[4] on the PClSt sample of molecular weight 3.8 × 10^5 in cumene showed that precipitation occured when the temperature of the solution decreased to several degrees below 59°C. The solution of the present sample, however, was soluble far below the θ-temperature and remained clear even at 40°C, partly because of its lower molecular weight compared with that of the previous sample. On lowering the temperature to approximately 30°C, the solution became translucent, but no precipitation was observed over several hours.

In *Figure 1*, the values of α and β plotted against temperature, respectively, show that there is no conspicuous trend suggestive of any influence of intra- and

Table 1 Dielectric polarization and dipole moment of poly-*p*-chlorostyrene in cumene

Temperature (°C)	α	β	p_2	P_2 (cc.)	μ(D)
25.0	1.697	0.2941	0.5512	76.39	1.36_6
30.0	1.640	0.2909	0.5445	75.46	1.36_0
40.0	1.591	0.2964	0.5375	74.49	1.36_4
50.0	1.483	0.2893	0.5242	72.64	1.35_0
55.0	1.448	0.2913	0.5185	71.85	1.34_4
65.0	1.344	0.2931	0.5011	69.45	1.31_6

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