Crystallizable Polyphenylacetylene. Electron Spin Resonance of Its Solutions

S. H. C. Chang,[1a] E. C. Mertzlufft,[1a] P. Ehrlich,* [1a] and R. D. Allendoerfer[1b]

Departments of Chemical Engineering and Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. *Received June 4, 1975*

ABSTRACT: Electron spin resonance was investigated in solutions of polyphenylacetylene made in the presence of ferric acetylacetonate and aluminum triethyl (PPA-C). The data were qualitatively similar to those obtained for solid PPA-C with respect to the saturation and temperature dependence of the signal. The concentration dependence of the unpaired spins was linear in the polymer concentration and extrapolated to the value reported previously for solid PPA-C. The concentration of unpaired spins per gram of polymer, N_s, at the reference temperature was independent of molecular weight for fractions in the range of $\overline{M_n}$ = 2200 to 5500 and corresponds to approximately 1 paramagnetic molecule in 200 at the reference temperature. It seems possible to view the paramagnetism of solid PPA-C and its solutions as an equilibrium property depending only on the structure and dynamics of the individual macromolecule.

Earlier work on thermally polymerized polyphenylacetylene (PPA-T)[2a] and polyphenylacetylene made in the presence of transition metal catalysts[2b–4] (PPA-C) had shown that the ESR signal observed in both of these forms of PPA was intrinsic to the molecular structure. A detailed study of PPA-C as a solid[2b] showed that, upon heating the "native" polymer, the concentration of unpaired spins (N_s) went through a maximum near the temperature at which an order–disorder transition took place, but that N_s stayed constant upon cooling (Curie dependence). It was suggested that the ESR signal was associated with single electrons in nonbonding orbitals and that the paramagnetic form of PPA could be represented by valence structures similar to those termed "bond-alternation defects" by Pople and Walmsley.[5] Yet, the physical basis of the Pople–Walmsley model could not be wholly applicable to PPA-C, because that model treats the paramagnetism as a reversible, purely electronic excitation, whereas the observations indicated irreversible structural changes in the polymer lattice.

It was hoped that studies on solutions of PPA, which like the solid have been known to be paramagnetic for a long time,[6] would lead to a better characterization of the paramagnetic structure. Exploratory work had led to a partial resolution of the hyperfine structure[3] of the single-line spectrum characteristic of both forms of PPA referred to, and of solutions of PPA-T in monomer. This report deals with the temperature, concentration, and molecular weight dependence of the paramagnetism of solutions of PPA-C.

Experimental Section

The whole polymer and its fractions were obtained by methods described.[4] The value of $\overline{M_w}/\overline{M_n}$ of each fraction was approximately 1.2. Samples for the ESR measurements were prepared and sealed on a vacuum line under exclusion of oxygen and in the presence of 0.5 atm of helium by methods similar to those applied to the solid polymer.[2b]

Most of the ESR measurements were carried out on a Varian E-9 spectrometer, coupled to a TE_{102} rectangular cavity with X-band detection at a modulation frequency of 100 kc. Incident power was monitored on a 432-C Hewlett-Packard power meter and the sample temperature was controlled by means of a Varian model E-257 variable-temperature controller. The signal was recorded in its first derivative representation. Several of the measurements were performed on the Varian Model 4502 spectrometer.

The sample tubes were kept in an oil bath for at least 16 hr prior to measurement at any one temperature and, subsequently, for 1 hr in the variable-temperature probe.

Results

In order to make as quantitative an estimate of the concentration of the unpaired spins, N_s, as possible, it is necessary to correct for saturation of the ESR signal and to take into account the hyperfine structure arising in most PPA solutions at about 100°C.[3] The former correction is applied in the same manner as for solid PPA-C. Figure 1 is an example of the saturation behavior of one of the solutions, where the reduced signal intensity, I_R, is defined by $Y'(m)P^{-1/2}$, where $Y'(m)$ represents the peak signal intensity of the first derivative spectrum and P represents the microwave power. The constant value of the ordinate at low power, I_{R_0}, multiplied by the density correction d/d_0 then represents N_s in arbitrary units. (As in the earlier work,[2b] it was found that, at the power levels in question, the line shape remained constant so that the peak signal heights provided an adequate relative measure of N_s where saturation was absent.) Under conditions where hfs became fairly well-resolved, the adequacy of this method was tested by drawing a line through the center of the hfs. Double integration of the best-resolved spectra at 100°C along the averaged line shape, and along the line including the hfs, showed that the possible error in estimating the total radical concentration by the former method does not exceed ½%. At higher temperatures, where the resolution was slightly better, the error may have been as large as 2%. This method was followed in calculating the magnitude of N_s for all spectra and thus represents only N_s of the major component, a radical with unresolved hfs. Note that the errors quoted refer to the precision, not the accuracy, of these results, which is estimated conservatively at ±20%.

Figure 2 represents the concentration of radicals, or unpaired spins, N_s, of a 5% solution in *p*-xylene of a PPA fraction of $\overline{M_n}$ = 5460. As with solid PPA-C,[2b] N_s goes through a maximum as a function of temperature, but the solutions show a Curie dependence upon cooling (signal proportional to $1/T$, characteristic of isolated spins). Fractions of $\overline{M_n}$ = 4200 and 3500 show qualitatively the same type of behavior with similar broad maxima in N_s in the vicinity of 100°C.

In order to determine the concentration and molecular weight dependence of N_s, samples were held for at least 16 hr in an oil bath at 100°C, the approximate temperature at which a broad maximum in signal occurred for all samples upon initial heating from room temperature. The concentration dependence of N_s is shown for several fractions up to weight concentrations of about 11%. With the exception of two measurements, all data can be represented by a straight line with intercept zero (Figure 3). Samples of unfractionated polymer also showed a linear concentration dependence over the broad concentration range of 1.5 to 25

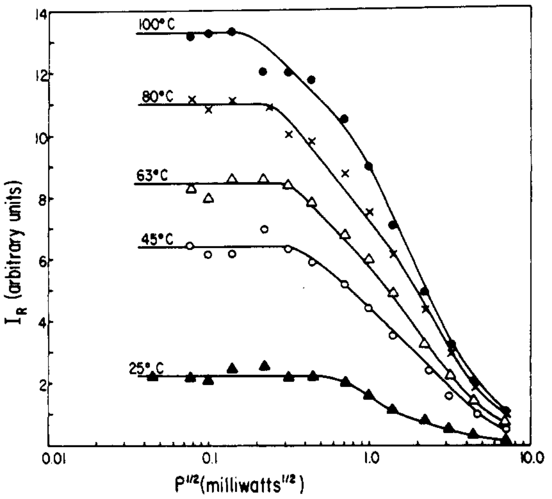

Figure 1. Reduced signal intensity, I_R, vs. square root of power for a 5% PPA, $\overline{M_n}$ = 5460 solution in xylene at 100°C.

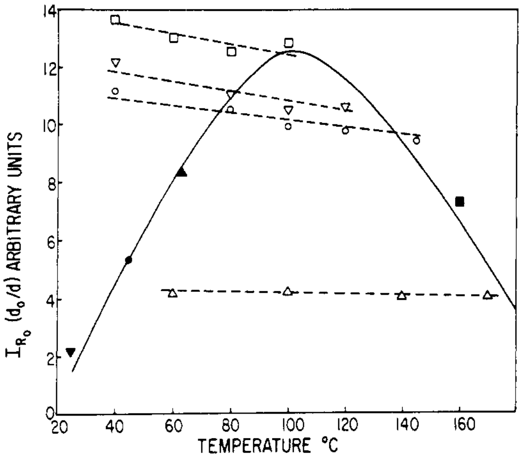

Figure 2. Relative spin concentration (unpaired spins/g PPA) of same sample vs. temperature (—) upon initial heating and (- - -) upon cooling. Filled symbols refer to heating curve; open symbols refer to the cooling curves; the open symbols furthest to the right on each cooling curve, at T = 100, 120, 145, 170, respectively, lie on the heating curve as well.

wt % polymer. In addition, extrapolation of the data of Figure 3 yields a value of 1.2×10^{18} spins/g for the pure polymer. The value measured for pure PPA is 1.0×10^{18} spins/g polymer.[2b]

One finds occasional statements by Russian workers to the effect that the concentration of unpaired spins in solutions of conjugated polymers is proportional to the polymer concentration and extrapolates to the value characteristic of the pure polymer,[6] and our data lend full support to this; the agreement between the measured and extrapolated values for the pure polymer are, in fact, better than would necessarily be expected for two different polymer preparations, taking into account all possible sources of error.

The constancy of N_s with the molecular weight (M) of the polymer is, however, in conflict with the behavior of PPA-T,[7,8] where N_s increases with M. The difference is probably attributable to the high molecular weight (absence of end effects) and greater steric regularity of PPA-C.

The value of N_s reported (1.2×10^{18} spins/g at 100°C) corresponds to 0.011 unpaired spins/molecule or, if the unpaired spins represent diradicals,[2b] one in 182 PPA molecules is paramagnetic.

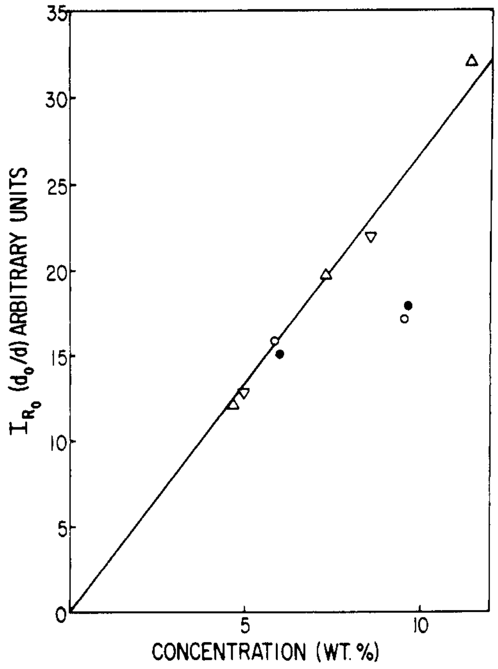

Figure 3. Relative spin concentration (unpaired spins/g solution) vs. polymer concentration (wt %) at 100°C for samples of different molecular weight: △, $\overline{M_n}$ = 2170; ●, $\overline{M_n}$ = 3500; ○, $\overline{M_n}$ = 4200; ▽, $\overline{M_n}$ = 5460.

Discussion

The qualitative similarity of the temperature dependence of solid PPA-C and its solutions, the linearity of N_s in the polymer concentration, and, if significant, the extrapolation of N_s with concentration to the value characteristic of solid PPA-C all indicate that the paramagnetism is a property which is attributable to the individual macromolecule. The rather good success in representing data from various fractions at different concentrations and with different preparative histories in the form of a single plot (Figure 3) allows us to view the paramagnetism of PPA-C as a reproducible equilibrium property, at least under the conditions characteristic of Figure 3. The constancy of N_s with molecular weight, furthermore, suggests that it might be possible to develop a quantitative structural theory of paramagnetism which need not take into account the chain ends. In the sense that N_s equals only 0.011 spins/molecule, the paramagnetism in PPA-C represents a "defect" property; although that term has been traditionally held to be reserved for the solid state physicist, defect models are being used increasingly to interpret the structure and properties of polyconjugated systems.[9] Because of the factors cited in the introduction, the bond-alternation defect model of Pople and Walmsley[5] does not do full justice to PPA-C. Other defect models that might account for paramagnetic polyconjugated systems have been discussed by Kventsel and Kruglyak.[10] Whichever of these models is most appropriate, the Curie dependence requires one to view the defect state as a ground state and not an electronic excitation as in the Pople–Walmsley model.

A considerable gap still exists between such simplified models of the electronic structure of linear conjugated chains and the structural detail the polymer scientist needs to know before he can specify a structure to his satisfaction. Since the complex temperature dependence upon initial heating of the ESR signal of PPA-C may well be associated with irreversible isomerization reactions, the determination of cis and trans structures surrounding skeletal double bonds would be valuable. Finally, one wonders whether the transformation from the diamagnetic state to the paramagnetic defect state may not play a role in the polymerization of all linear PPA and might not, in fact, be responsible for the rather low molecular weight of all polymers of acetylene derivatives.[4] Research to resolve these problems is in progress.

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References and Notes

(1) (a) Department of Chemical Engineering; (b) Department of Chemistry.

(2) (a) P. Ehrlich, R. J. Kern, E. D. Pierron, and T. Provder, *J. Polym. Sci., Part B*, **5**, 911 (1967); (b) G. M. Holob, P. Ehrlich, and R. D. Allendoerfer, *Macromolecules*, **5**, 569 (1973).

(3) P. Ehrlich, R. C. Mertzlufft, and R. D. Allendoerfer, *J. Polym. Sci., Polym. Lett. Ed.*, **12**, 125 (1974).

(4) M. Biyany, A. J. Campagna, D. Daruwalla, C. M. Srivastava, and P. Ehrlich, *J.Macromol. Sci., Chem.*, **9**, 327 (1975).

(5) J. A. Pople and S. H. Walmsley, *Mol. Phys.*, **5**, 15 (1962).

(6) A. A. Berlin, *J. Polym. Sci.*, **55**, 621 (1961).

(7) A. Bendersky, B. Y. Kogan, V. F. Gashkovsky, and I. E. Shlapnikova, *Karbotsepnye Vysokomol. Soedin. 1963*, 253 (1963).

(8) P. Ehrlich, *J. Macromol. Sci., Phys.*, **2**, 153 (1968).

(9) D. Bloor, D. J. Ando, F. H. Preston, and G. C. Stevens, *Chem. Phys. Lett.*, **24**, 407 (1974).

(10) F. Kventsel and T. A. Kruglyak, *Theor. Chim. Acta*, **12**, 1 (1968).

The Configuration Partition Function, a priori Probabilities, and Conditional Probabilities for Branched Macromolecules Subject to the Rotational Isomeric State Approximation[1]

Wayne L. Mattice

Department of Biochemistry, Louisiana State University, Baton Rouge, Louisiana 70803.

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ABSTRACT: Procedures are presented for computing the configuration partition function for branched macromolecules which are subject to the rotational isomeric state approximation. The assumptions required are (1) the short-range interactions can be adequately represented by three- and four-bond interactions, (2) bond lengths and bond angles are constant, and (3) there are a minimum of two bonds between each branching point. A molecule with any number of branches can be treated. Procedures are also presented for the computation of a priori and conditional bond probabilities. Illustrative calculations are carried out for a low-density polyethylene containing *n*-butyl groups.

Many configurational properties of linear chain macromolecules have been successfully treated by application of the rotational isomeric state approximation.[2,3] Branched chain molecules have not previously been treated with similar precision, although this class of polymer molecules is of considerable interest. Naturally occurring examples of such macromolecules include proteins in which disulfide bonds serve to cross-link different polypeptide chains. Many polysaccharides also exist as branched chain molecules. The objective here is to extend the methods developed[3] for linear chain molecules subject to the rotational isomeric state approximation so that they can also be applied to branched chain molecules. The terms treated are the configuration partition function, a priori probabilities, and conditional probabilities. The symbolism and procedures used by Flory[3] will be adopted, and extensions and modifications will be introduced where necessary.

Definition of the Polymer Chain

A macromolecule consisting of a main chain plus one branch is shown diagrammatically in Figure 1. Side chains are not included in this figure and will not be treated here. The macromolecule in Figure 1 can also be viewed as consisting of three branches which emanate from the atom at which branching occurs, and this viewpoint will be adopted henceforth. The branch selected as "branch 1" will be chosen arbitrarily. Branches 2 and 3 will then be assigned by requiring that $n_2 \geq n_3$, where n_j is the number of bonds in branch j. All n_j will be assumed to be greater than unity. The bonds in branch 1 are numbered sequentially, starting with the bond which is most remote from the branching point. Bonds in branches 2 and 3 will also be numbered sequentially, but in these cases numbering will commence at the branching point and proceed to the remote termini of these branches. The symbol ${}_j\mathbf{l}_i$ represents the vector for bond i in branch j and ${}_j\phi_i$ represents the rotation about bond i in branch j. Bond angles and bond lengths will be considered to be constant. The atom designated ${}_j\mathrm{A}_i$ is located at the terminus of bond vector ${}_j\mathbf{l}_i$. The first atom in branch 1 is ${}_1\mathrm{A}_0$.

Statistical Weight Matrices

A particular chain conformation is specified by assigning values to all ${}_j\phi_i$ except ${}_1\phi_1$, ${}_2\phi_{n_2}$ and ${}_3\phi_{n_3}$. The reference state will have a trans conformation for all of the bonds about which rotation must be specified. Special attention must be given to the meaning to be attached to "trans" for bonds involving ${}_1\mathrm{A}_{n_1}$. Those atoms specifying the conformation at the last bond in branch 1 will be ${}_1\mathrm{A}_{n_1-2}$, ${}_1\mathrm{A}_{n_1-1}$, ${}_1\mathrm{A}_{n_1}$, and ${}_2\mathrm{A}_1$. The state at the first bonds in branches j (j = 2 or 3) will be specified by atoms ${}_1\mathrm{A}_{n-1}$, ${}_1\mathrm{A}_n$, ${}_j\mathrm{A}_1$, and ${}_j\mathrm{A}_2$. Bond n_1 in branch 1 and the first bonds in branches 2 and 3 are in the trans conformation as shown in Figure 1.

The statistical weight matrix for bond i in branch j is