Hyperelectronic Polarization in Polymeric Semiconductors

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Electronic conduction properties of organic materials were first reported by Pochettino in 1906, in a study of the photoconductivity of anthracene. It was some 40 years later that investigators began seriously examining organic materials. Within recent years, many organic solids (well over 100) have been examined and classified as semiconductors.

Of particular interest is a group of polymeric semiconductors which exhibit unusually high dielectric constants. This is certainly not to be expected, since polyethylene and polytetrafluoroethylene, among other such polymers, possess dielectric constants of 2.3 and 2.9 respectively.

Pohl and Rosen (1965) first reported this phenomenon of high dielectric constants. Further evidence of the effect was reported by Rosen and Pohl (1966) and by Hartman and Pohl (1965).

Since that time we have found several additional polymers which exhibit such a phenomenon. This paper presents data for 4 of these polymers. In addition a model which qualitatively accounts for the unusually high dielectric constants is presented and discussed.

SAMPLE PREPARATION

The polymers were prepared and purified in a manner similar to that described by Pohl and Engelhardt (1962) and Pohl, Bornmann, and Ito (1962).

Polymers JM77B and JM85B were formed by mixing zinc chloride and anthracene with pyromellitic dianhydride (PMA) 1:1:1, and zinc chloride and phenothiazine with mellitic trianhydride (MTA) respectively, and heating at 295 C for a period of 24 hr under nitrogen (Mason, Pohl, and Hartman 1967).

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Sample DP1A was prepared by mixing anthraquinone with PMA 1:1:1 and zinc chloride as a catalyst, and heating 24 hr at 300 C.

SK3A polymer was prepared by mixing N,N'-dimethyldithiooxamide with copper sulfate (1:1) (Hartman, Kanda, and Pohl, 1966).

Each of the polymers studied was a fine-grained, black, insoluble powder. After formation the powders were purified by continued washing in hot water, ethanol, and toluene in a Soxhlet apparatus. Following purification, they were stored in a desiccator until used.

DIELECTRIC CONSTANT MEASUREMENTS

The audiofrequency dielectric constants were determined by measuring the parallel capacitance of the samples in a Bridgman opposed-anvil high pressure cell. (For specific details of the cell, cf. Rosen and Pohl, 1966.) A Koop's bridge (Koop, 1951) was employed to measure the capacitance of the sample, after the background capacitance had been carefully nulled out. This bridge has an advantage over most bridges in that it yields the parallel capacitance and resistance of the unknown directly.

Before taking data, the samples were premolded at high pressures (~20,000 Kbar) to insure good compaction of the polycrystalline materials.

Data obtained on sample JM77B is displayed in Figure 1. The resistivity remains essentially constant, while the dielectric constant is approximately halved, over the frequency range examined.

Similar characteristics are exhibited by polymers DP1A and JM85B as shown in Figures 2 and 3 respectively.

Polymer SK3A departs from the above generalization, as can be seen in Figure 4, in that the resistance drops significantly as well as does the dielectric constant.

Table I presents general data for the polymers studied, listed in order of increasing dielectric constant. The values tabulated correspond to a frequency of 1 KHz.

In addition to frequency dependence, the dielectric constant dependence upon applied pressure and electric field strength were studied. Data is not presented here, but the general trend was that the dielectric constant increased with pressure, and decreased with increasing electric field strength. The latter observation agrees with that reported by Rosen and Pohl (1966).

DISCUSSION OF RESULTS

In general, a solid dielectric will exhibit various types of polarization when exposed to an alternating electric field. There are four distinct types of polarization known. These mechanisms are shown graphically in Figure 5. Each form of polarization plays an important role in determining the dielectric properties of a solid within its respective frequency range. A given solid will possess one or more of these dispersions in its dielectric constant, the number depending upon the structure of the solid.

The particular range of interest to this study centers around the 1 KHz value. This corresponds to the range normally associated with surface polarization phenomena. However, if one examines the curves shown in Figures 1-4, it is obvious that there is a tremendous enhancement in dielectric constant over that for most hydrocarbons ($\epsilon_r \sim 2$-6). In addition, there is no trend for the dielectric constant to level off below 1 KHz. In fact, it appears to swing upward at a very fast rate.
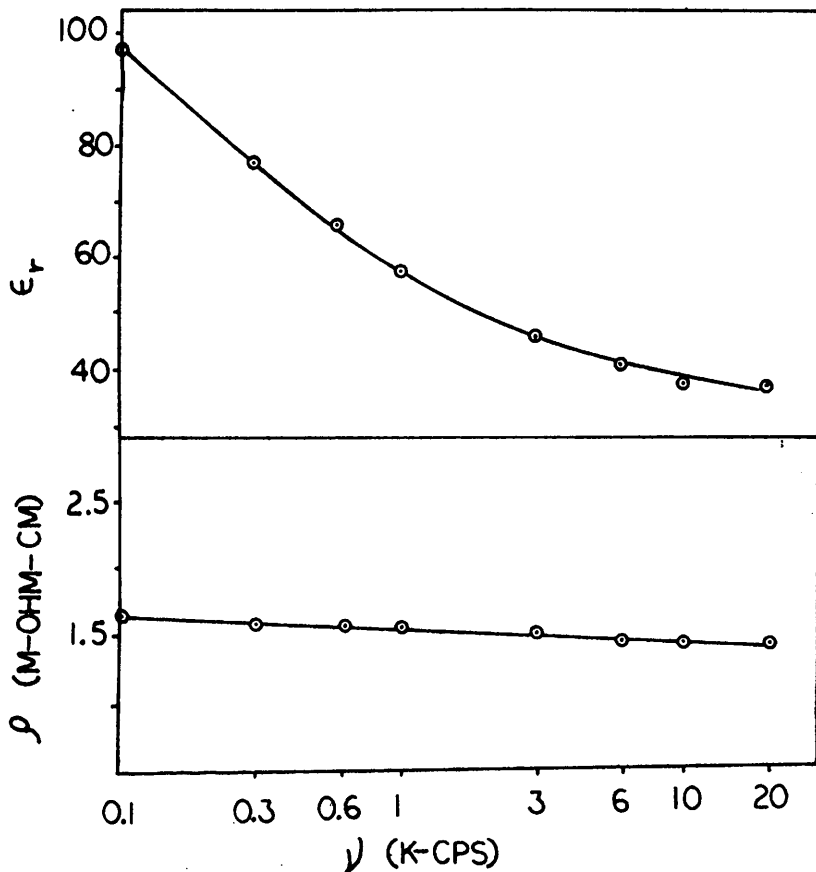
Figure 1.   Variation of the relative dielectric constant (ϵ_r) and resistivity (ρ) for the polyacene quinone radical polymer based on anthracene and pyromellitic dianhydride, versus frequency; $T = 298$ K, $P = 1.37$ Kbars.
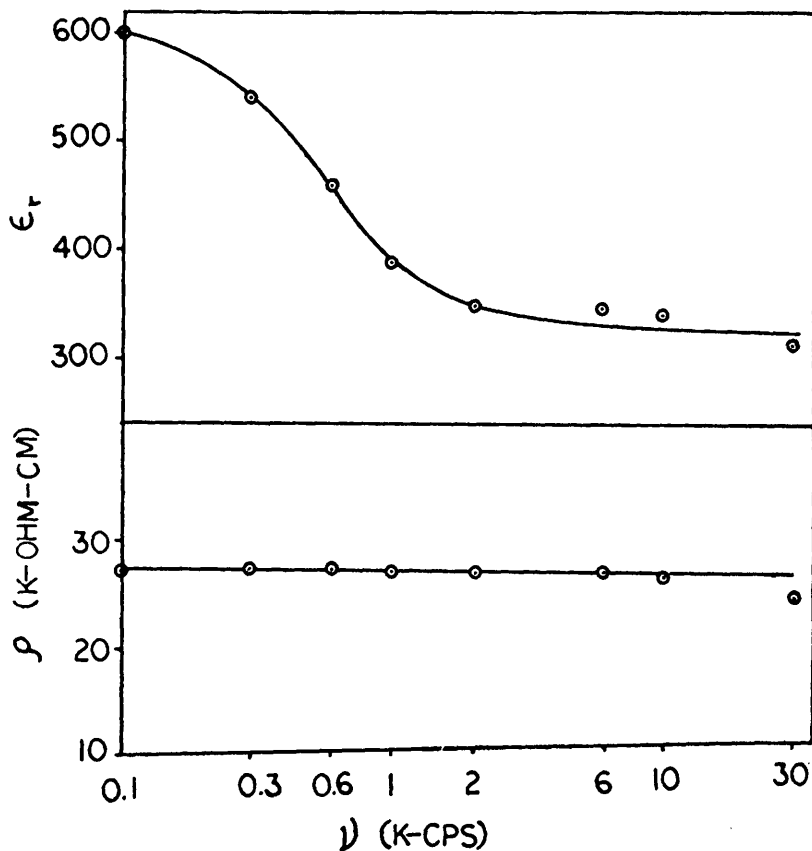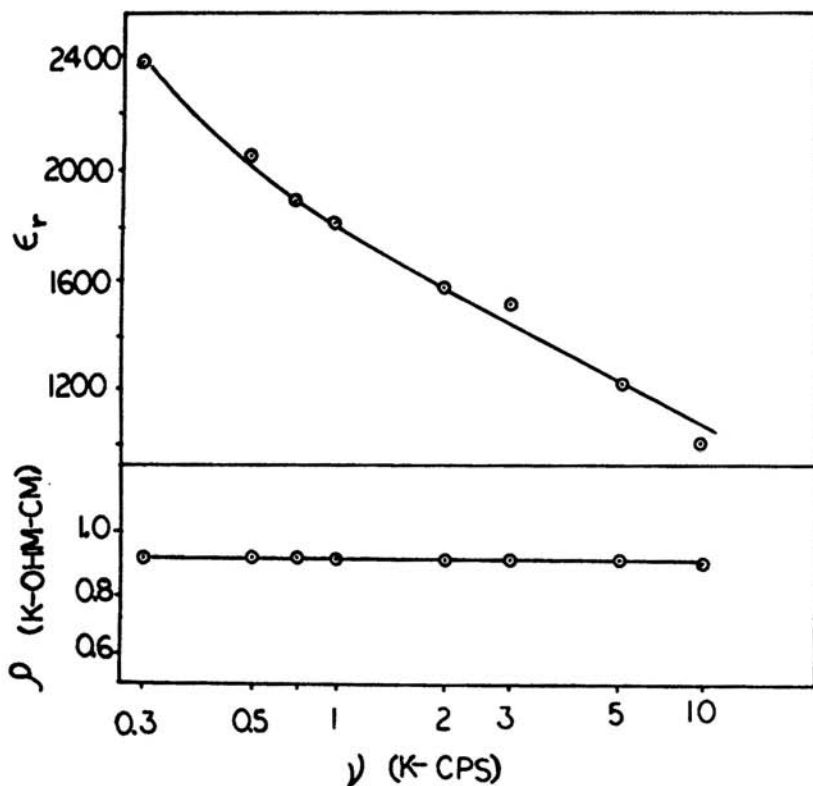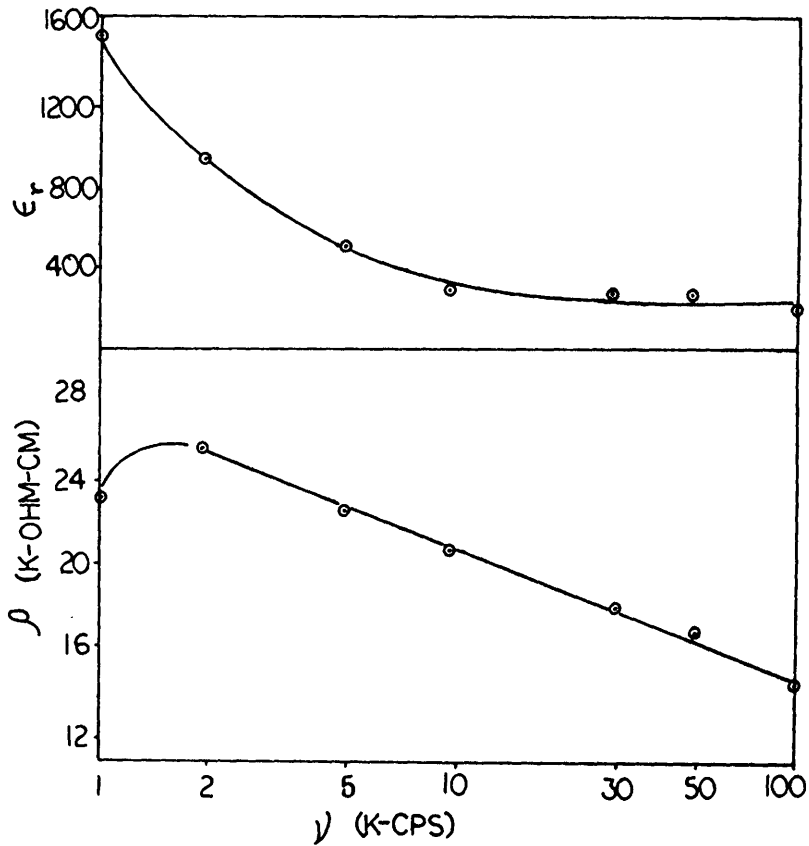
Figure 2. Variation of the relative dielectric constant (ε_r) and resistivity (ρ) for the polyacene quinone radical polymer based on anthraquinone and pyromellitic dianhydride, versus frequency; $T = 298$ K, $P = 1.1$ Kbars.

Figure 3. Variation of the relative dielectric constant (ε_r) and resistivity (ρ) for the polyacene quinone radical polymer based on phenothiazine and mellitic trianhydride, versus frequency; T = 298 K, P = 1.37 Kbars.
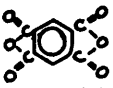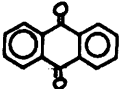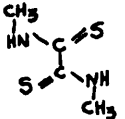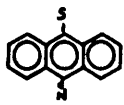
Figure 4. Variation of the relative dielectric constant (ε_r) and resistivity (ρ) for the metallo-organic complex polymer based on Cu^{++} and N,N'-dimethylrubeanic acid (i.e., copper N,N'-dimethylrubeanato polymer), versus frequency; T = 298 K, P = 7.85 Kbars.

TABLE I

PARAMETERS FOR POLYMERIC SEMICONDUCTORS[a]

Sample No.	Chemical Composition	Resistivity (ohm-cm)	Dielectric Constant (relative to ϵ_o)
JM77B	Anthracene PMA[b]	1.6×10^6	58
DP1A	Anthraquinone PMA[b]	$2.7 \times 10^{5[d]}$	390[d]
SK3A	N,N - Dimethyl Rubeanic Acid	$2.35 \times 10^{4[e]}$	1550[e]
JM85B	Phenothiazine MTA[c]	9.5×10^2	1820

(a) Unless otherwise noted, data reported is for the sample at room temperature (298°K) under a pressure of 1.37 Kbars with the frequency of applied electric field being 1 KHz.
(b) PMA: pyromellitic dianhydride.
(c) MTA: mellitic trianhydride.
(d) Measured at pressure of 1.1 Kbars.
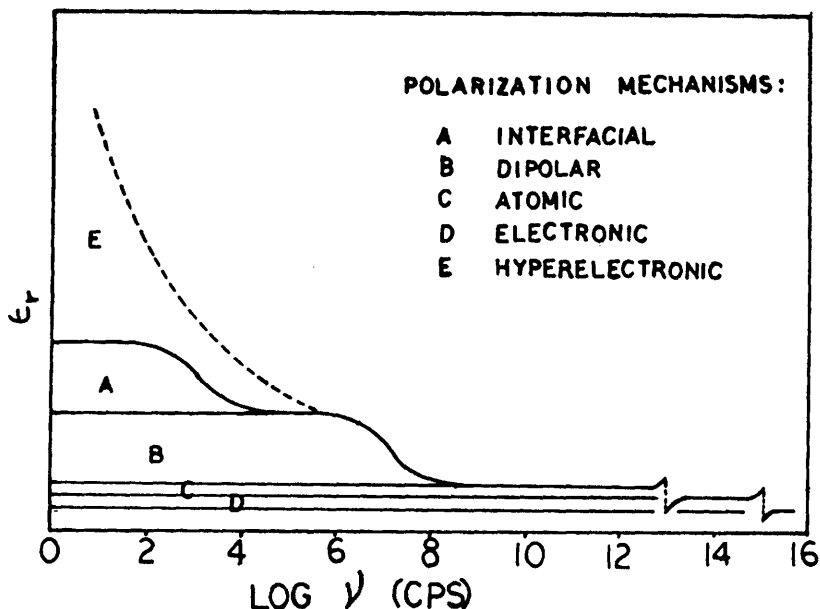(e) Measured at pressure of 7.85 Kbars.

Figure 5. Variation of the relative dielectric constant (ε_r) with frequency for a general solid dielectric. Each relaxation depends upon the mechanism as labeled. The new type of polarization, hyperelectronic polarization, is shown by the dashed curve.

This phenomenon, shown qualitatively in Figure 5 as a dashed line, has been designated as "hyperelectronic" polarization. Its origin is thought to be due to the formation of extremely large dipoles which oscillate within the sample when an alternating electric field is applied.

In order to discuss this phenomenon of hyperelectronic polarization, let us consider a typical polymeric semiconductor as being composed of long ellipsoidal molecules as shown in Figure 6(a). Note the dimensions of the molecules. The length has been suggested by Pohl and Englehardt (1962) and Rosen and Pohl (1966), while the diameter corresponds to a carbon-carbon bond length.

Further we shall consider the sample as possessing some degree of localized molecular ordering or stacking. Now, imagine a thermally produced carrier pair (e^- and e^+) to be formed at the position indicated by (*). Each carrier migrating through the solid finally becomes localized in the two molecules as shown. The carriers are depicted within the brackets, so as to indicate that there is some average domain in which the carriers may be found when no electric field is applied.

Upon applying an alternating electric field, the electron will migrate in one direction, while the hole migrates in the opposite direction (Figure 6(b)). The molecule itself is assumed to possess virtually no resistance. Thus, the carriers very quickly move to opposite ends of their respective molecule, and form an oscillating dipole. This dipole will be very large in magnitude, due to the large molecular dimensions which constitute the dipole arm.
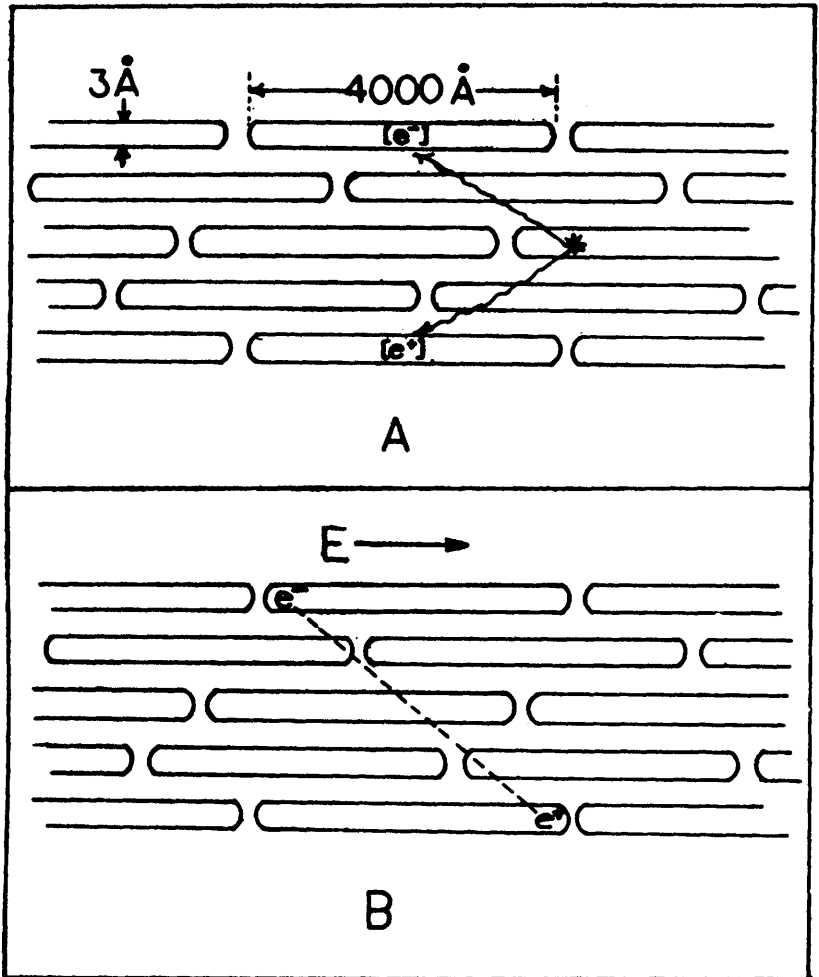
Figure 6.   Representation of molecules within a polymeric semiconduc-
            tor, showing localized ordering. (A) Without an electric field,
            there is no net polarization. (B) With an electric field, a
            large dipole is produced which gives rise to the large polariza-
            tion observed.

       Hence, this "hyperelectronic" polarization is thought to be the cause
of the unusually high dielectric constants observed in some polymeric
semiconductors.   It appears analogous to the surface polarization effects
of Maxwell-Wagner (Von Hippel, 1954) but is thought to be microscopic
in nature rather than macroscopic.

SUMMARY

Extremely high dielectric constants, observed in polymeric semiconductors, have been attributed to a phenomenon called hyperelectronic polarization, which is thought to result from the formation of a very large dipole within the polymer. The dielectric constant is observed to be: (1) inversely proportional to frequency; (2) inversely proportional to applied electric field strength; and (3) directly dependent upon pressure. All of these findings, excepting the latter, verify earlier findings by Rosen and Pohl (1966).

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