Ambient Pressure Measurements of the Dielectric Properties of Poly (Acenequinone) Radical Polymers

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The dielectric properties of powdered poly(acenequinone) radical polymers (PAQR) were investigated under ambient pressure conditions using a specially designed sample holder. The study utilized dielectric and conductivity measurements over an intermediate frequency range (10^2-10^5 Hz) with the temperature and the DC electric field bias on the sample taken as variable parameters. The activation energies and the average molecular lengths show good agreement with existing models and theories on the conduction process in these polymers.

INTRODUCTION

PAQR polymers are black, powdered, long-chain aromatic compounds prepared by the condensation of monomers of the anthrone or anthracene types as well as pyrene, or chloroanthraquinone types, with aromatic anhydrides using $ZnCl_2$ as a catalyst. The preparation of these polymers has been described (1). These polymers have very unusual properties such as relatively high dielectric constants, very long relaxation times (on the order of 10^{-4} s), a unique characteristic behavior in the presence of an externally applied DC electric field bias, and an unusually high ratio of AC to DC conductivity (2). Most of these properties have been discovered while the polymers were under elevated pressures that avoid problems arising from their powdered state (3-8).

This report presents an account of dielectric and conductivity measurements performed on a select group of PAQR polymers. These measurements were successfully done for the first time under ambient pressure conditions. A specially designed chamber/sample holder module, with very low background capacitance, was constructed to conduct these measurements.

The temperature dependence of the conductivities allowed the determination of the activation energies, while the frequency dependence of the AC conductivity resulted in the value of the exponent S in the empirical formula $\sigma_{AC} \propto \omega^S$. The dependence of the DC conductivity on the DC electric field bias showed perfect agreement with the empirical formula already established by Rosen and Pohl (5) and yielded parameters which enabled the determination of the average molecular lengths for these polymers.

EXPERIMENTAL METHODS

To conduct dielectric measurements on prepressed samples from the powdered polymers under ambient pressure, a special chamber/sample holder was constructed with a variety of provisions for studies of dependence of properties on temperature and DC electric field. The main idea behind the design was to hold the sample between the capacitance plates of the measuring module under a predetermined amount of contact pressure that is accurately reproducible.

These requirements were met in an all brass chamber shown in Fig. 1. The principle of operation is based on the constant pressure C-clamp design of Chester and Jones (9). In this modified adaptation, the addition of a guard electrode (G) was incorporated as an integral part of the chamber body to lower its overall capacitance. Three hard vinyl screws (S) keep the "hot" electrode mount (M) fixed in place by attaching it to the top section of the guard electrode frame (F). Two steel side screws (N) lock the shaft (V) in its right position once the proper tightening pressure on the polymer sample (P) is attained. The capacitance module itself features a removable high-voltage electrode (A) that fits via a shoe mount (O) onto the shaft (V) of the main advancement screw. The greatest advantage of this design is that the whole chamber (with the hot capacitance plate (A) removed) may be regarded as part of the background capacitance. Thus, the total capacitance equals the background plus the capacitance of the module holding the dielectric sample (2, pp. 69-70).
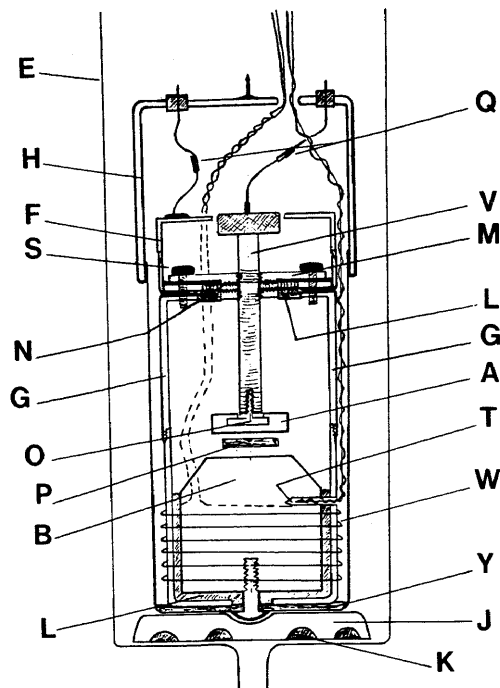
Figure 1. Cross-sectional view of the chamber and sample holder module.

TABLE 1. The dielectric constant (ϵ_r), the loss factor (*DM*) and the total conductivity σ' at four frequencies for five PAQR polymers. The units for σ' are $10^{-7}(\Omega\bullet cm)^{-1}$.

Polymer Code	Property Measured	Frequency / Hz			
		10^2	10^3	10^4	10^5
LD-104	ϵ_r	52.0	24.0	9.8	6.2
	DM	0.7	0.6	0.6	0.3
	σ'	2.1	8.5	37.0	95.0
LD-97	ϵ_r	58.0	26.0	12.0	7.2
	DM	1.2	0.7	0.6	0.3
	σ'	3.7	9.5	40.0	115.0
LD-95	ϵ_r	53.0	18.0	8.0	5.3
	DM	1.2	1.0	0.6	0.2
	σ'	3.5	10.0	28.0	64.0
LD-94	ϵ_r	36.0	25.0	13.0	6.2
	DM	5.2	2.0	0.8	0.5
	σ'	21.0	28.0	55.0	170.0
LD-14A	ϵ_r	58.0	12.0	5.9	5.3
	DM	0.5	0.8	0.4	0.1
	σ'	1.3	5.5	13.0	30.0

TABLE 2. The AC and DC activation energies[a], the exponent *S*, the DC conductivity, the average molecular length, and the ratio of AC to DC conductivity at 1 kHz for five PAQR polymers.

Code	E_{AC}	E	S	σ	L_o	σ'/σ
LD-104	0.17*	0.29	0.58	1.7	118.0	500
LD-97	0.14*	0.30	0.52	3.2	111.4	290
LD-95	0.14	0.25	0.43	3.7	67.0	280
LD-94	0.12	0.21	0.41	25.0	43.0	130
LD-14A	0.12	0.25	0.46	0.68	70.0	695

* Values obtained at 10 kHz; other values of E_{AC} were obtained at 1 kHz.
[a] Units are: E_{AC} and E, eV; σ, $10^{-9}(\Omega\bullet cm)^{-1}$; L_o, nm.

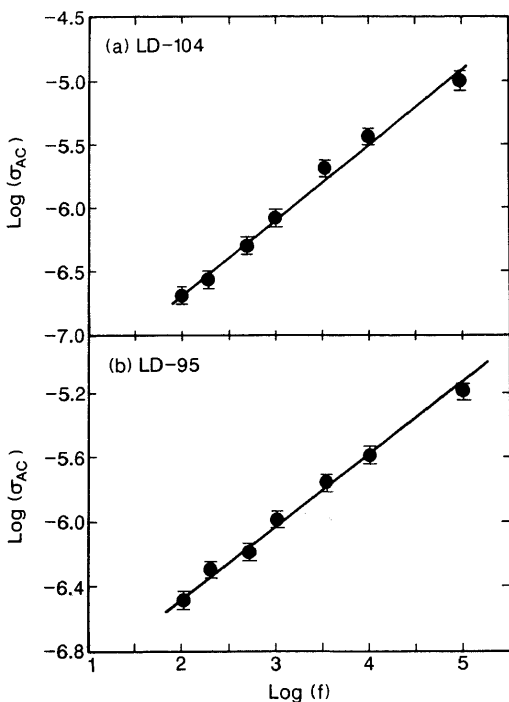A thermocouple junction (T) is fitted on the side of the anvil to monitor the temperature accurately to within ±2 K. A 105-W heater (W) encases the lower half of the anvil. A pyrex glass enclosure (E) allows us to control the environment around the sample for either a nitrogen flow or vacuum.

The techniques used in the measurement of the capacitance with loss are the ones employing a standard impedance bridge. For our purpose, a General Radio (Schering type) impedance bridge Model 716-C operating in the series mode was used. The system also employed a guard circuit Model 716-P4. The adaptation of the Schering bridge to perform impedance measurements under DC electric field bias has been discussed in the literature (2, pp. 84-86). DC conductivity measurements were conducted using a Keithley DC electrometer in series with a standard 10-V regulated power supply.

The dielectric samples were prepared in the form of pellet-shaped discs by compressing a Teflon ring filled with the powder between special carbide anvils to a pressure of 2.5 kbar using a hand-operated hydraulic press. This eliminated voids in the samples.

The PAQR polymers were made by combining 1,2,4,5-benzenetetracarboxylic dianhydride, $ZnCl_2$, and an aromatic component in 1:1:2 mole ratio; the aromatic component was violanthrone for production of LD-97 and LD-104, anthracene for LD-95, and pyrene for LD-94. LD-14A was made by combining 19.42 g of anthrone and 300 g of polyphosphoric acid. Details of the syntheses are available in references 1, and 2 (pp. 103-104).

RESULTS AND DISCUSSION

The polymers studied in this research exhibited the typical low-frequency relaxation characteristic of eka-conjugated systems (4,6). The greatest drop in the value of the dielectric constant always occurred around 10^3-10^4 Hz (Table 1). The data were obtained from measurements on pre-pressed

Figure 2. The frequency dependence of the AC conductivity for (a) LD-104 and (b) LD-95.
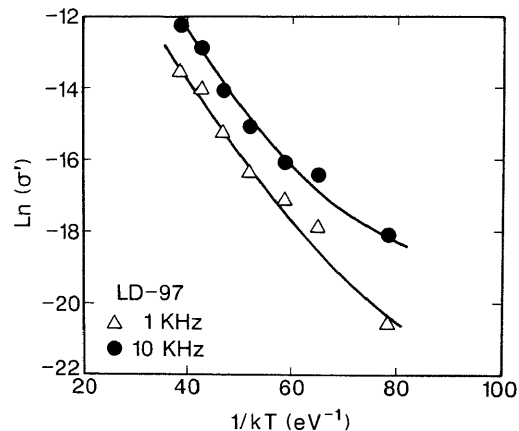

Figure 3. Temperature dependence of the AC conductivity of LD-97 at 1 kHz and 10 kHz.

Figure 4. Temperature dependence of the DC conductivity of LD-97.

pellets at room temperature and pressure over a frequency range of three decades (10^2 - 10^5 Hz). The frequency response of the AC conductivity, σ_{AC}, displayed the well known power law $\sigma_{AC} = B_O \omega^s$, where B_O is a constant and the exponent S is between 0.40 and 0.80 (Table 2). These values of S are an indication that the relaxation times are widely dispersed, which is a consequence of the amorphous nature of these materials (10). Fig. 2 shows a typical frequency response of the AC conductivity for polymers LD-104 and LD-95. The straight lines in the figure are the best linear fit derived from a least squares method. The exponent S in Table 2 is determined from the slope of these curves.

The activation energies, denoted as E_{AC} and E for AC and DC conduction respectively, are also given in Table 2. Generally, these are obtained from the semilogarithmic plots of the real part of the AC conductivity and the DC conductivity, σ, versus $(kT)^{-1}$. The activation energy is then determined as the absolute value of the average slope of the approximate straight line in the resulting plot. However, for these particular polymers it was found that the total conductivity, $\sigma' = \sigma_{AC} + \sigma$, is much greater than σ. Therefore, we are justified in plotting σ' instead of σ_{AC}; it is σ' which is directly measured while σ_{AC} is obtained as σ' - σ.

In Fig. 3, the total conductivity is plotted versus $(kT)^{-1}$ for two different frequencies as obtained from the polymer LD-97. The average slopes of the curves in this figure corresponding to the frequencies 1 kHz and 10 kHz are 0.14 ± 0.02 eV and 0.17 ± 0.02 eV, respectively. We note from the plot in Fig. 3 that the AC activation energy is independent of the frequency of the measurement and has been observed to be the case over the frequency range studied (10^2 - 10^5 Hz). This is expected on theoretical grounds since the activation energy, whether AC or DC, represents the net contribution of several energies, such as energy gaps and potential energy barriers, which are independent of frequency. Figure 4 shows a typical behavior of the DC conductivity versus $(kT)^{-1}$ for LD-97. A comparison of Figs. 3 and 4 shows
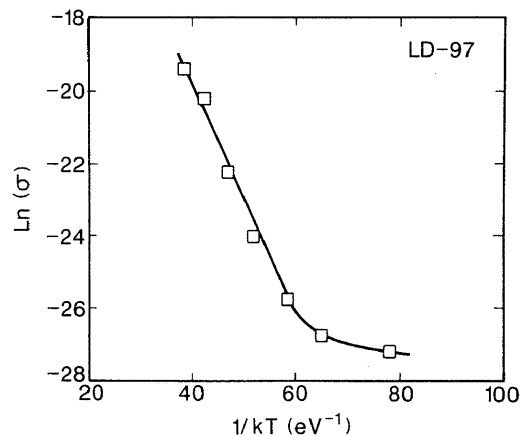
an appreciable difference between the magnitudes of these two conductivities.

Table 2 gives a summary of the basic results obtained from the five polymers studied. Included in this table are the average molecular lengths derived from the dependence of σ on the DC electric field bias given by the Rosen-Pohl formula (5), whereby a linearized plot is used to determine these values very accurately for each of the five polymers studied (2, pp. 225-235).

Most of our reported results contained about an 8-12% standard deviation in both the dielectric constant (ε_r) and the loss factor (DM). The DC conductivity had an average error of 8% resulting from the combined errors in the electrometer readings and the calculation of the geometry of the sample. Moreover, reproducibility of the results on any given polymer was within the experimental margin of error.

In Table 2, it is no coincidence that the data for LD-104 and LD-97 are similar. These two samples are separate preparation batches of the same polymer but disguised under different code names to verify the reproducibility of the measurements as well as that of the chemical process.

The measurements obtained under ambient pressure have shed new light on some of the properties of these polymers. The most interesting observation from this research is that the ratio of the AC to DC conductivity is quite large (Table 2). This phenomenon would be somewhat obscured in high-pressure measurements because the DC conductivity increases much faster with pressure than the AC conductivity (2, pp. 144-190). Hence, the ratio decreases and becomes less apparent at high pressures.

This research has provided important information concerning the ambient pressure properties of these polymers which is needed in determining their potential electrical engineering applications.

ACKNOWLEDGMENTS

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