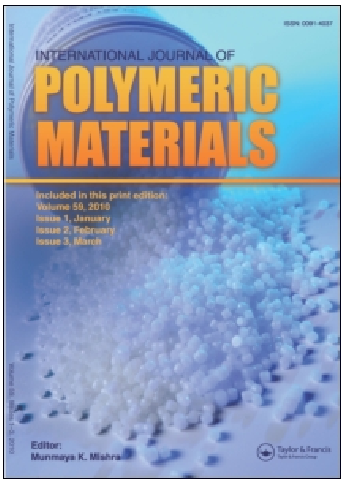

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S. Abdul Jawad[a]; M. Bader[b]
[a] Department of Physics, Faculty of Science and Arts, The Hashemite University, Zarqa, Jordan [b] Department of Chemistry, Pennsylvania State University, Pennsylvania

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AC ELECTRICAL BEHAVIOR OF A NOVEL AROMATIC ELECTRO-OPTIC POLYIMIDE

S. Abdul Jawad
Department of Physics, Faculty of Science and Arts,
The Hashemite University, Zarqa, Jordan

M. Bader
Department of Chemistry, Pennsylvania State
University, Pennsylvania

AC electrical behavior of a novel aromatic electro-optic polyimide was investigated in the temperature range 25°C to 300°C and covers frequency range from 1 Hz to 10^6 Hz. Three electrical quantities, ac impedance, conductivity and permittivity were reported. The experimental results show that the relative permittivity of aromatic electro-optic polyimide is temperature independent below 200°C, indicating that the chains below this temperature are nearly rigid. Above this temperature a relaxation process was observed with an activation energy 35 KJ/mole associated with a restricted rotational motion of the side chain chromophore.

Keywords: impedance, permittivity, relaxation, activation energy

1. INTRODUCTION

Significant progress in synthesizing and processing of polymers has led to preparation of new materials with a favorable mechanical, thermal, optical and electrical properties. These developments, along with theoretical advances have led to increasing knowledge of structure-property relations. Development of polymers based on aromatic structure, led to high performance polymers with high thermal and electrical stability. An intensive research work was performed on this class of polymers in order to relate the structure to physical and mechanical properties. The development of polymers as structural materials focused attention on the consideration of change of polymer physical properties with temperature

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Address correspondence to S. Abdul Jawad, Department of Physics, Faculty of Science and Arts, The Hashemite University, P.O. Box 150459, Zarqa 13115, Jordan.

and frequency. Polyimides emerged as promising candidates for electro-optic applications. A new class of a highly stable aromatic polyimides with electro-optic and photo-refractive properties has been reported. An intensive work has been published concerning the synthesis [1] and properties [2] of these materials. The interest behind this is the potential applications of these materials in three-dimensional holographic, light processing, phase conjugation and the handling of large quantities of information in real time [3, 4].

In the past few years, two approaches have been used to prepare electro-optic and photo-refractive polymeric materials, namely, the composite material and the fully functionalized polymers [5 – 7]. Investigation of the dielectric relaxation provides a powerful tool for studying the effects of temperature and frequency on the above mentioned properties. For instance, dielectric relaxation spectroscopic measurements were performed on refractive polymers [8] to investigate the changes in molecular dynamics during bulk polymerization of an epoxide-amine system [9]. In addition, dielectric relaxation was also used to study relaxations in second-order nonlinear optical materials [10 – 12]. In this paper the ac electrical behavior of a novel only electro-optic polyimide will be reported as a function of frequency and temperature.

2. EXPERIMENTAL

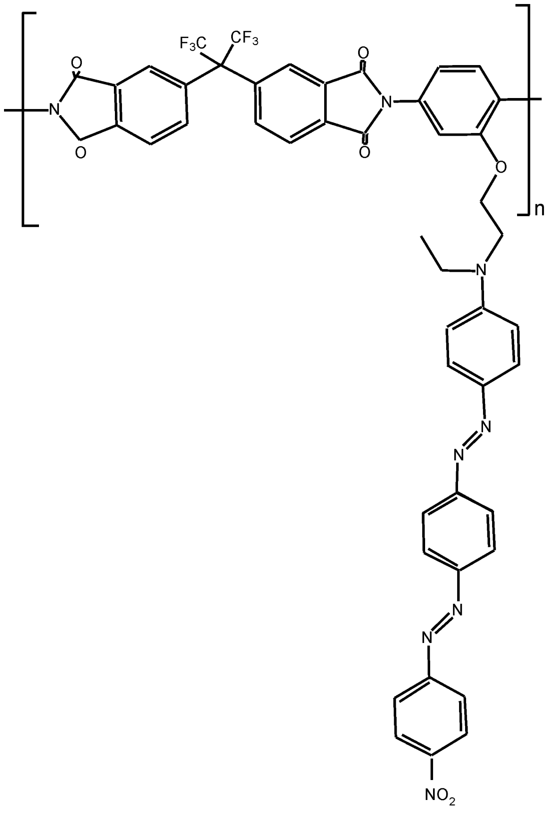
2.1. Materials

The polymer used in this study was prepared according to a procedure similar to that described by Yu *et al.* [13]. We stress here that the elemental analysis and spectroscopic data for the synthesis polymer indicate its high degree of purity and the absence of any inorganic ionic impurities. Elemental analysis results for the synthesized polymer were as follows:

Calculated: $C_{45}H_{30}N_8O_7F_6$;C60.52;H3.2;N12.01.

Found: C60.27;H3.29;N11.95.

The polymer film was cast on indium tin oxide (ITO) glass with thickness 6.16 µm. Its number average molecular weight M_n is 27,000 and the weight average M_w is 42,000. The material is thermally stable, where no degradation was seen in FTIR spectra after heating to 300°C. A good reproducibility of the measured data was obtained after heating and cooling cycles. The structure of the polymer is shown in Scheme 1.



SCHEME 1

2.2. AC Measurements

The ac impedance measurements were carried out in the temperature range 20 – 300°C, and covering a frequency range 1 Hz to 10^6 Hz, using a Solarton – 1260 Impedance/Gain Phase Analyzer (Schlumberger Instrument). The instrument is controlled by software packages provided by the manufacture which maximize the performance and data handling of the system. Aluminum was evaporated on the surface of the film. The samples set-up was then kept in a shielded cavity to improve low frequency measurements. Best signal generator amplitude and dc bias were selected after performing a series of amplitude and dc bias sweeping tests. Then for the measurements 0.5 V for amplitude and zero dc bias were chosen. Using this set-up, ac complex impedance Z^* and the phase angle (θ) were measured. From the measurements of Z^* and (θ), the real and imaginary components of ac-impedance (Z^*), permittivity (ε^*) and conductivity were determined and plotted as function of frequency at different temperatures.

3. RESULTS AND DISCUSSION

Using ac impedance measurements, it is possible to identify the various regions of the polycrystalline samples. Equivalent circuit consisting from resistive (R) and capacitive (C) elements represent the grain boundary, the bulk and electrode regions. These regions might appear as a series of semicircles in the plot of the imaginary (Z'') and the real (Z') components of the complex ac impedance. The analysis of ac impedance is represented in Refs. [14–20].

Figure 1 presents the plot of Z' *versus* frequency respectively at different temperatures. Below 200°C, Z' increases with decreasing frequency without showing any plateau region while the phase angle remains negative over the

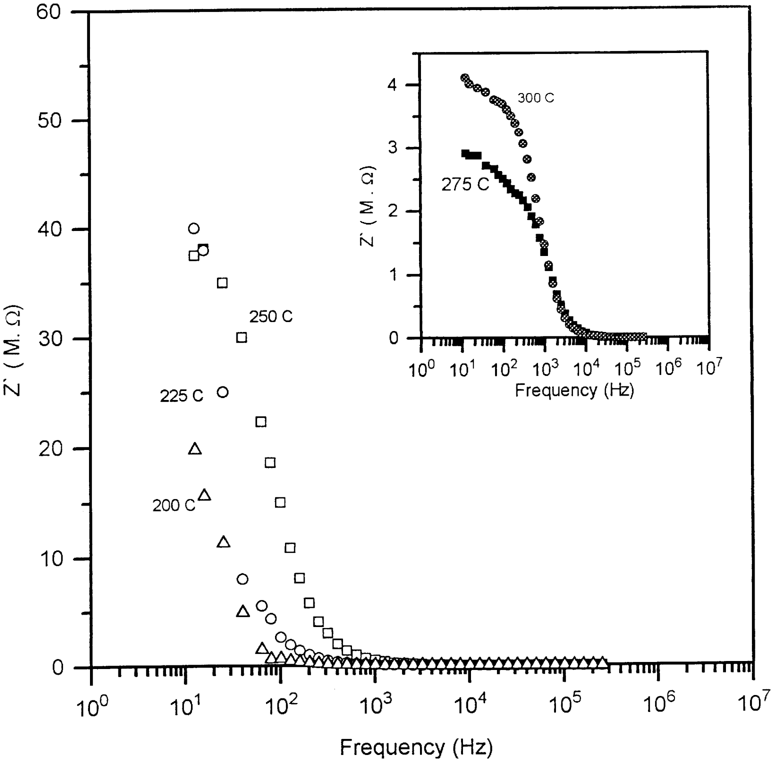


FIGURE 1 Real component of ac impedance (Z') *vs.* frequency at different temperatures for a novel aromatic electro-optic polyimide.

measured frequency range. However, above 200°C the observed curves for the real component of ac impedance and phase angle is similar to that observed in $R-C$ network in parallel, where Z' is independent of frequency at low frequency range and then becomes proportional to the inverse of frequency. Therefore the bulk material at temperature above 200°C can be considered to consist of capacitive and resistive components in parallel, with ohmic behavior dominant at high temperatures and low frequencies. Using ac impedance analysis at temperature above 200°C where the material can be represented as RC networks in parallel, the equivalent bulk resistance and capacitance can be found. The bulk resistance at 200°C is in the order of 3.29×10^8 ohm and decreases to 2.34×10^6 ohm at 300°C as given in Table 1. On the other hand the capacitive component of the equivalent circuit at temperatures 225°C and above remains nearly without appreciable change.

Figure 2 shows the dependence of ac conductivity on temperatures at two frequencies 1 kHz and 1 MHz. At 1 kHz no plateau region was observed over the measured temperature range, while at 1 MHz a plateau region starts to appear at temperature below 200°C, indicating that the material has high electrical stability below 200°C, where no relaxation peak was observed below 200°C in the plot of Z'' *versus* frequency. However, above this temperature a relaxation peak started to appear and became a well defined peak at 225°C as shown in Figure 3 supporting our conclusion that the chains are nearly frozen in a rigid structure at temperature below 200°C. The relaxation peak moves to a higher frequency with increasing temperature. This peak is observed when $\omega_{\max}\tau = 1$, where τ is the apparent relaxation time. With increasing temperature, τ decreases and therefore, the relation will be satisfied at higher frequency. Nevertheless, the dependence of the relaxation time is generally assumed to take the Arrhenius form,

$$\tau = \tau_0 \exp -\Delta E/\mathrm{R}T$$

where, E is the apparent activation energy, τ_0 is the relaxation time at infinite temperature, T is the absolute temperature and R is the gas constant. The relaxation time is taken to be the reciprocal of the experimental

TABLE 1 Equivalent bulk resistance and capacitance for a novel aromatic electro-optic polyimide sample

Temperature °C	*R* (Ω)	*C* (*Farad*)
225	3.29×10^8	1.97×10^{-10}
250	4.29×10^7	5.58×10^{-11}
275	3.76×10^6	5.50×10^{-11}
300	2.43×10^6	2.43×10^{-11}

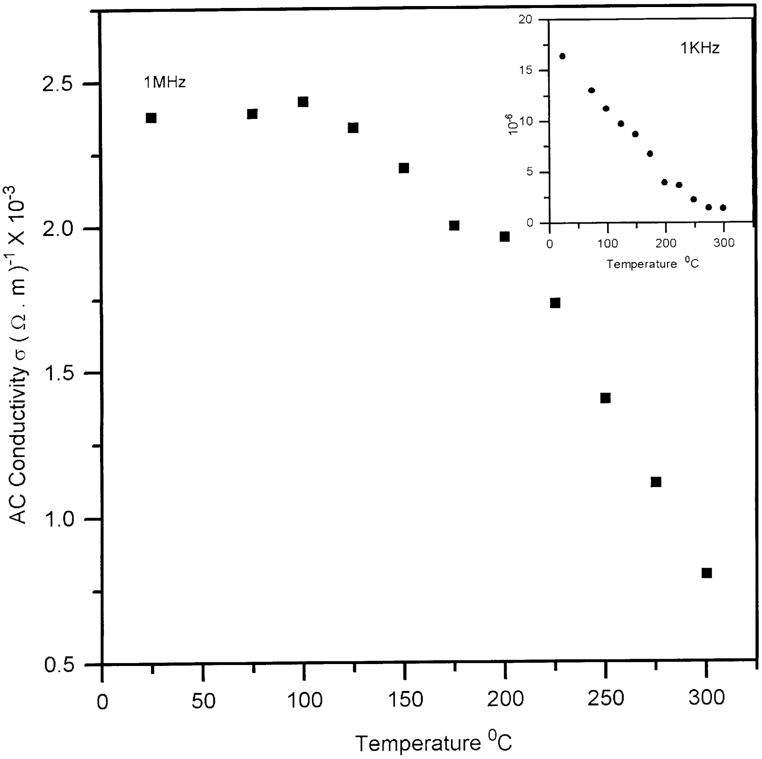


FIGURE 2 AC conductivity (σ) *vs.* temperature at 1 kHz and 1 MHz for novel aromatic electro-optic polyimide.

frequency ω_{max} at which the dielectric loss factor or the mechanical loss factor exhibit a maximum. The apparent activation energy was obtained from the plot of $\log f$ *versus* $1/T$, where f is a frequency at maximum Z'' where, the maximum frequencies of the relaxation peaks coincide with one another. The activation energy was calculated to be about 35 KJ/mole which is comparable to the activation energy of gamma process as a result of a rotational motion of a side chain liquid crystalline polymers [21, 22]. We point out that the calculated activation energy for our samples is less than that assigned to full rotational motion of backbone polar groups in liquid crystalline copolymers for which the activation energy is in the order of 125 KJ/mole [23, 24]. Therefore, we believe that the observed relaxation process in our sample is more likely due to highly restricted rotational local motion of the side chain chromophore.

It is important to note that the relaxation peaks in Z'' are broad which can be assigned to be as a result of relaxation occurring within the bulk

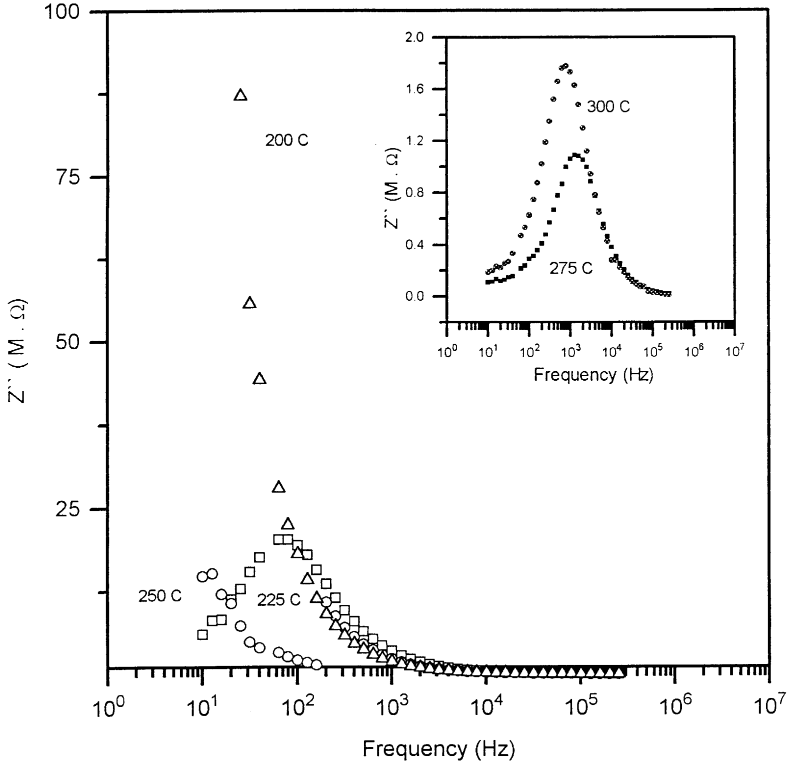


FIGURE 3 Imaginary component of ac impedance (Z'') *vs.* frequency at different temperatures for novel aromatic electro-optic polyimide.

materials. This has been verified by plotting Z'' *versus* Z' as shown in Figure 4. At temperatures 275°C and 300°C an almost perfect semi-circle with a tail is observed. The perfect semi-circle can be assigned to the restricted local motion of the side chain chromophore as described above. The tail can be associated with some sort of phase separation similar to the effect of grain boundaries in polycrystalline materials with rather small activation energy.

The real component of permittivity is nearly independent of frequency at temperatures below 200°C. Increasing the temperature results in sharp change in the real component of permittivity at low frequencies, as shown in Figure 5. The strong frequency dependence of ε' at low frequencies and high temperature indicates that the interfacial polarization contributes significantly to the polarization in the sample at low frequencies. However, interfacial polarization arises wherever phases with different conductivities

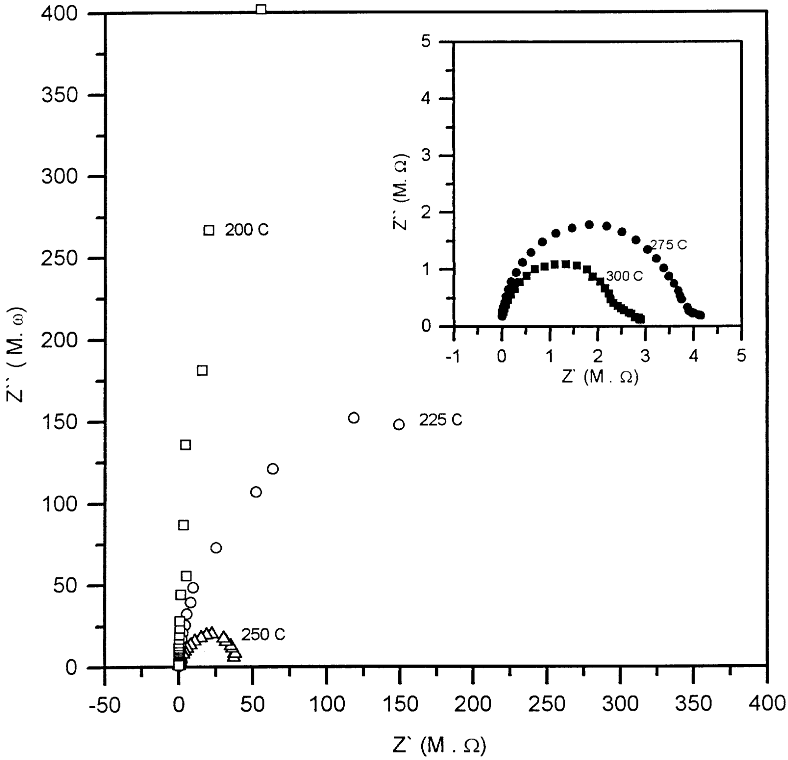


FIGURE 4 Imaginary component (Z'') *vs*. real component (Z') of ac impedance at different temperatures for novel aromatic electro-optic polyimide.

are present. This may results from the formation of different micro-regions with varying conductivities, so if this is the case, it may be the reason for observing a distorted semi-circle at low frequencies in the plot of Z' *versus* Z''.

Finally, we can conclude that the constancy in ac impedance, dielectric permittivity and conductivity up to 200°C indicates that the electro-optic polyimide exhibit very high stability in dipole configuration. This may suggests that the mobility of the side chain is highly restricted to a limited localized motion. At 200°C, which represents a threshold temperature for this polymer, the mobility of the side chain chromophore starts to increase in a way to affect the electrical behavior of the material. These findings concerning thermal stability of electrical behavior of this polymer makes it a favorable candidate for electro-optic applications.

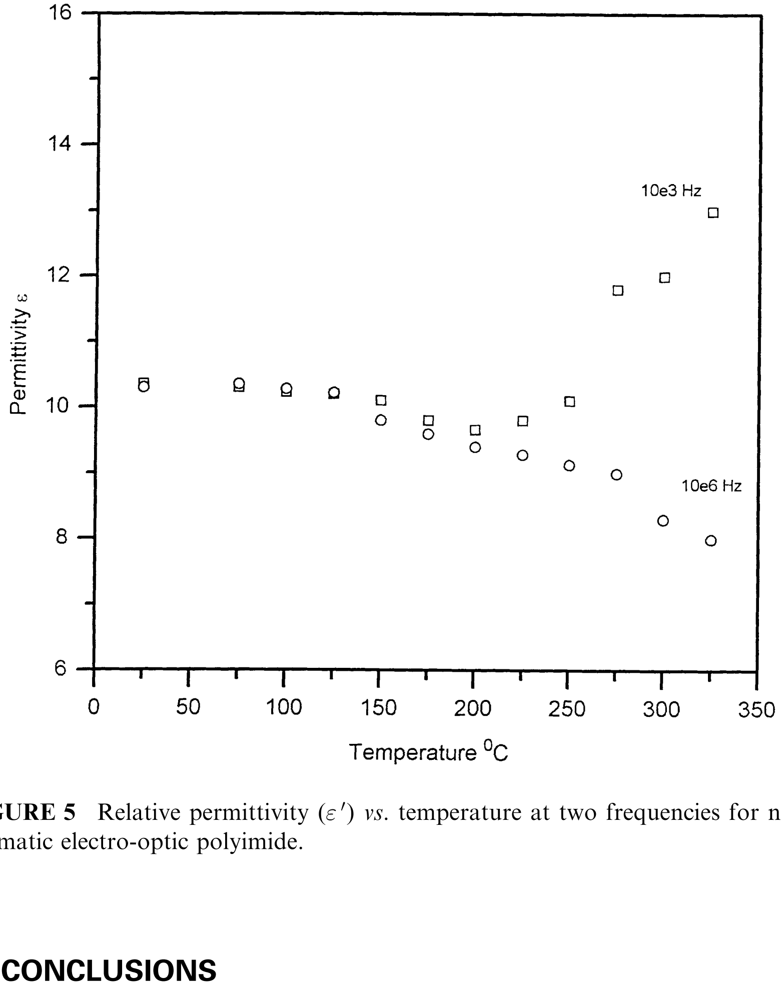


FIGURE 5 Relative permittivity (ε') *vs.* temperature at two frequencies for novel aromatic electro-optic polyimide.

4. CONCLUSIONS

The present study investigates the dependence of electrical behavior of a novel aromatic electro-optic polyimide on temperature and frequency. The experimental results reveal the following conclusions:

1. The electro-optic polyimide shows high thermal stability below 200°C due to high rigidity of polymer chains. This result clearly demonstrates and strengthens the notion that the suitability of such polymeric materials and related structure for electro-optic applications.
2. The main relaxation process in this system has an activation energy of 35 KJ/mole associated with a restricted local rotational motion of side chain chromophore.

3. The mobility of the polymer chains increases above 200°C and is associated with a dramatic change in electrical behavior of the polymer with a sharp increase in dielectric constant at low frequencies.

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