Study of ferroelectricity in polyaniline

A. A. Bahgat[a]; S. M. Sayyah[b]; H. M. Abd-Elsalam[b]

[a] Physics Department, Faculty of Science, Al-Azhar University, Cairo, Egypt [b] Chemistry Department, Faculty of Science (Beni-Suef Branch), Cairo University, Beni-Suef City, Egypt

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STUDY OF FERROELECTRICITY IN POLYANILINE

A. A. Bahgat
Physics Department, Faculty of Science, Al-Azhar University, Cairo, Egypt

S. M. Sayyah
H. M. Abd-Elsalam
Chemistry Department, Faculty of Science (Beni-Suef Branch) Cairo University, Beni-Suef City, Egypt

Polymerization of aniline (ANI) was achieved in aqueous medium using sodium dichromate as oxidant in presence of hydrochloric acid. The obtained polyaniline was characterized by X-ray diffraction and electron microscopic studies. The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) results were used to study thermal degradation of the polymer. The unusually high dielectric constant of the produced polyaniline gives an indication for the important dielectric properties of the prepared PANI. The present study confirmed the observation of ferroelectricity of the prepared polyaniline with a Curie's temperature at 323 K. This observation is unique concerning this polymer which has the advantage of being prepared at room temperature. The ferroelectric phenomenon of this conducting polymer was confirmed by studying pyroelectricity, (P-E) hysteresis loop and polarization as a function of temperature.

1. INTRODUCTION

Polyaniline, PANI, has been extensively studied in the last decade as an electrically conducting polymer which shows many promising properties. Fast switching rates [1, 2], the ability to switch reversibly from insulating to conducting state either by electrochemical or chemical doping [3, 4] and their unique optical properties are some of

PANI potential applications. Several review papers on polyaniline have been published recently [5−7]. PANI and its blends are new in the following aspects:

- their conductivity is metallic, more precisely: comparable with mesoscopic metals.
- in the galvanic series, PANI and its blends are positioned closely below silver.
- thin layers (3 to 50 μm) are transparent, although green, with conductivity values between 10^{-9} to 10^{-1} S/cm; at higher conductivity, only very thin layers (below 3 μ) are semitransparent.
- PANI and its blends are electro- and chemochromic (*i.e.*, they change color upon application of a certain voltage or appropriate chemicals); they also change their conductivity together with these chemical changes: green/metallic; blue/neutral base/insulating; colorless/reduced state/insulating.
- the three reproducibly accessible oxidation states connected with the three colors can be accessed also in blends and can serve as different states of PANI in catalytic processes.

Based on these properties specific for PANI, applications are actually on their way to the market or may be realized in further developments.

Moreover, PANI has been extensively studied because it is the only known conjugated polymer with a chain in which nitrogen instead of carbon atoms bridges the benzenoid and quinoid rings and playing an important role in the π-bond formation and the electrical interaction conduction consequently.

In protonated polyaniline, PPANI, the addition of protons by a protonic acid such as HCl leaves the number of electrons in the $-N=$ chain unaltered [3] while causing a great increase in conductivity from 10^{-10} to 10^2 S/cm at room temperature. On the other hand, the dc conductivity of polyaniline is thermally activated and follows the expression $\sigma(T) = \sigma_o \exp[-(T_o/T)^n]$ where T is the temperature, T_o is a constant and n = 1/4 or n = 1/2, where the second value being common in pressed powder samples. In conducting polymer such as PANI and polyaniline derivatives, the conduction is highly modulated by variety of parameters such as presence of free carriers (electrons, protons and ions), formation of polaron lattice of the material, and energy band asymmetry which is determined by the composition and structure of the given polyaniline. In such polymers the conduction mechanisms and charge carriers can be varied from free electron conduction to hopping, passing though an ionic conduction [8, 9].

Various chemical oxidizing agents such as potassium dichromate, potassium iodate, ammonium persulphate, hydrogen peroxide, ceric nitrate and ceric sulphate have been used for the chemical oxidative polymerization of aniline [6]. Several research groups have been engaged in investigating polymerization mechanisms and reaction kinetics of aniline in aqueous solutions [11−19]. Generally, it is agreed that the initiation reaction involves the formation of a radical cation intermediate and the subsequent combination of two radicals' cations to form the aniline dimer. After this initial step, the method by which these species proceed to form polymer is still not clearly understood, but different mechanisms have been reported for this growing step.

The morphology of synthesized PANI [20] was studied after dedoping and redoping with dedocylbenzenesulphonic acid (DBSA) and polystyrene (PS). Also, the temperature-conductivity dependence of soluble polyaniline films doped with DBSA has been studied [21]. The effect of molecular weight of PANI doped with lithium hexa-fluorophosphate on the d.c. conductivity temperature dependence was reported [22].

The effect of pH of the polymerization solutions or the effect of acid concentration, reaction time, relative and absolute reactant concentrations on the polymer yield, chemical composition and the electrical conductivity of the produced polyaniline were investigated [23−25].

Aniline oligomers of different degrees of oxidation have been synthesized and their structures were determined by ^{1}H- and ^{13}C-NMR and infrared spectroscopy [26]. The chemical polymerization conditions of polyaniline synthesized with different oxidizing agents and the physicochemical properties were studied [27].

Water soluble polyaniline was prepared and extensively studied by X-ray diffraction, X-ray photoelectron spectroscopy XPS, electronic spectroscopy, infrared spectroscopy IR, thermogravimetric analysis TGA, conductivity measurements, atomic force microscopy and scanning tunneling microscopy [28]. Further study of the chemical polymerization of m-toluidine, o-chloroaniline and nitroaniline by DSC, X-ray, IR, XPS and conductivity measurements were performed [29]. It was found that the substituted group of aniline affects not only the polymerization reaction but also the properties of the polymers obtained. HCl-doped emeraldine form of polyaniline (PANI-H) was synthesized by oxidative polymerization of aniline in aqueous hydrochloric acid solution using potassium dichromate as an oxidant [23]. Furthermore kinetics of the chemical polymerization of 3-methylaniline, 3-chloroaniline and 3-hydroxyaniline in aqueous solution were

characterized by IR, UV-visible, X-ray, electron microscope, TGA, DTA and a.c. conductivity were investigated [30−32].

In the present study the electrical properties of the oxidized polymerization of aniline in aqueous hydrochloric acid medium using sodium dichromate as oxidant were investigated. Techniques such as X-ray diffraction, electron microscopy, thermal analysis, a.c. conductivity, polarization, ferroelectric hysteresis and pyroelectric current measurements were applied to characterize the obtained polymer. The present study confirmed the observation of ferroelectricity of the prepared protonated polyaniline, PANI. This present observation is unique concerning this polymer which has the advantage of being prepared at room temperature.

2. EXPERIMENTAL

2.1. Material Preparation

Aniline, which was vacuum distilled before being used, and sodium dichromate were supplied by Merck Chemical Company (Germany). Concentrated hydrochloric acid, sulphuric acid and ammonia (33%) were of chemically pure grade products provided by Prolabo-Chemical Company (England). Double distilled water was used as a medium for the polymerization reactions during the present work.

The polymerization reactions were carried out in a stoppered conical flasks of 250 ml capacity containing the amount of monomer (ANI) followed by the addition of sodium dichromate solution (25 ml) to the reaction mixture under nitrogen atmosphere. The order of addition of substances was kept the same in all experiments. The stoppered conical flasks were then put in an automatically controlled thermostat at the required temperature. The flasks were shaken (15 shakings/10 seconds/every 15 minutes) for definite periods of time. The reaction was stopped by the addition of ammonia solution (in equimolar amount to HCl) and cooling in ice bath. The polymer was then filtered using Buchner funnel, washed thoroughly with distilled water, methanol and finally dried in vacuum oven at 60°C till constant weight. In case of polymer samples prepared for characterization, after three polymerization hours the solutions were filtered after the addition of (30 ml) methanol as nonsolvent, then washed with distilled water, air dried and finally dried under vacuum at room temperature to constant weight. The polymerization of distilled aniline (0.2195 g · mol/L) in 25 ml of HCl having different concentrations in the range (0.40 to 1.00 g · mol/L), was carried out by the addition of 25 ml sodium dichromate solution (0.0293 g · mol/L) as oxidant under

nitrogen atmosphere at 5˚C for different time intervals. The concentration of both HCl and oxidant is reduced to half of its initial values after addition of oxidant solution to the acidified monomer solution. The concentration of aniline and oxidant are kept constant at 0.1097 g · mol/L and 0.0146 g · mol/L respectively.

The aqueous polymerization of aniline (0.2195 g · mol/L) in 25 ml (0.4 g · mol/L) HCl solution and 25 ml of sodium dichromate solution which has a morality of 0.0073 g · mol/L as oxidant under nitrogen atmosphere at 5˚C for different time intervals was carried out. The total concentration of both HCI and monomer were fixed in the reaction medium at 0.2 and 0.1097 g · mol/L respectively. The final product was air dried and finally was completely dried under vacuum at room temperature. Extended preparation procedure and chemical characterization of PANI are given elsewhere [30−32].

2.2. Thermal Analysis

The thermalgravimetric analysis, TGA, and differential thermal analysis, DTA, of the polymer sample were performed using a thermal analyzer (SH1MAZU DT-30). The weight loss from the TGA was measured from ambient temperature up to 550˚C with heating rate of 20 K/min. The weight loss of the sample was calculated as function of temperature to determine the degradation rate of the polymer. Different transition temperatures were determined from the DTA thermograms.

2.3. Electron Microscopy and X-ray Diffraction Analysis

The electron microscopic analysis was carried out using JSM-T20 Scanning electron microscope, JEOL, Japan. While the X-ray diffraction was obtained using a Philips, 1976 Model 1390 diffractometer using Cu (K_α) radiation.

2.4. Electrical Measurements

Polymer samples in the form of compressed discs of 1.0 cm diameter and 0.2 cm thick were used in the present investigation. Good contact was attained through covering the samples on both sides with air drying electric conducting silver paste. The a.c. measurements of the electrical conductivity and dielectric constant were performed using a computerized Stanford Research CRL bridge (SR-720 CRL) at the

frequency range $0.12-10^2$ kHz and over the temperature range $30-150°C$. The overall error in the a.c. conductivity did not exceed $\pm 2\%$.

Polarization, P, as a function of applied electric field, E, hysteresis loop was studied applying Sawyer-Tower [34] circuit at constant frequency of 70 Hz. Polarization was measured at different applied electric fields and temperatures. On the other hand, pyroelectric current was traced as a function of temperature using HP 610 electrometer employing the two-probe method on short circuit setup. The temperature was monitored using K-type thermocouple with $\pm 0.2°C$ accuracy.

3. RESULTS

3.1. Elemental and Thermal Analysis

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of protonated polyaniline, PPANI are shown in Figure 1. Form the TGA curve, it is clear that the first step at 69°C, is due to the dehydration of water molecules (4-H_2O) present in the polymer structure [30–32]. This stage was completed at 119.16°C (with a midpoint at 85.9°C) while the corresponding weight loss is 14.6%. However, the dehydration of water molecules from the polymer structure shows an endothermic peak in the DTA thermogram in the temperature range 38.4–177.3°C, with a peak maximum at 50°C (323 K) and heat change of -759.2 J/g. The second step on TGA curve is observed in the temperature range 274.5–366.7°C (with midpoint at 336°C) corresponding to the loss of 2 HCl molecules present on the two imine nitrogen atoms in the polymeric chain. The weight loss in this stage is found to be 15.0% as compared with the calculated one 14.4%. The last step on the TGA curve (in the range 367.8–470°C) is due to complete decomposition of the polymeric chain. The weight loss in this case amounts to 50.1% while the calculated loss is found to be 50.69%. The above stages give exothermic peaks on the DTA thermogram at T_x and T_d as given in Table 1, indicating crystallization and decomposition temperatures, respectively. These two peaks follows a weak endothermic band starting at $T_g = 216°C$, describing a glass transition temperature. Further results concerning this preparation are presented elsewhere [30–32]. The endothermic peak starting at 472°C indicates melting of the final charring material without any further decomposition up to 550°C as shown from the TGA as well, see Figure 1.
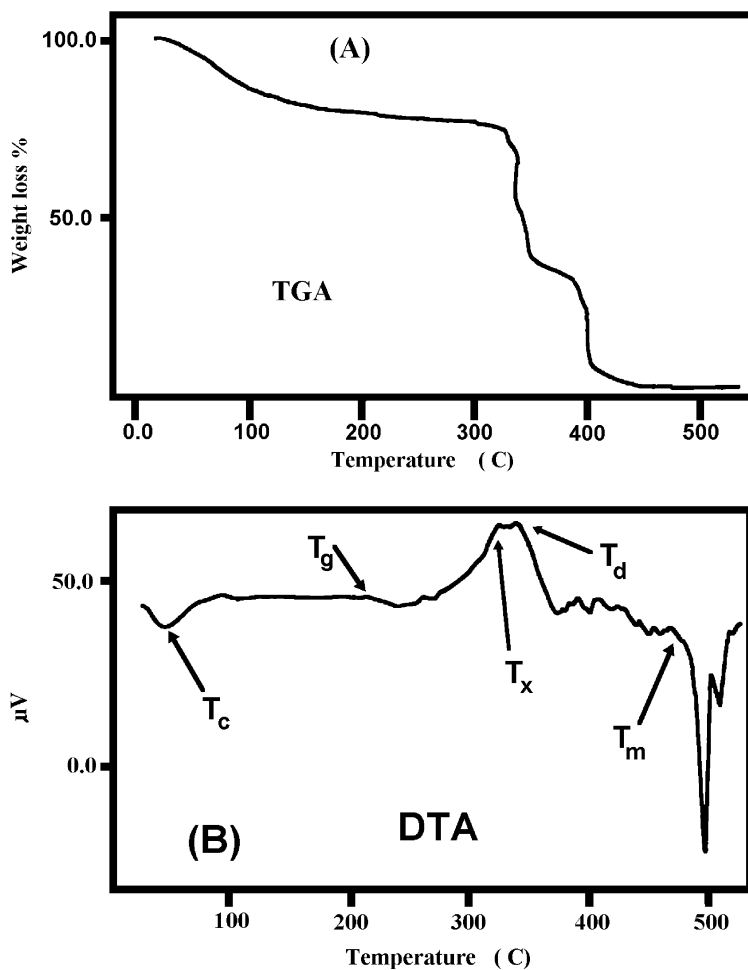
FIGURE 1 Thermal analysis of PPANI, (A) TGA and (B) DTA.

TABLE 1 Important Transition Temperatures of Polyaniline in K, Extracted from DTA Thermogram

T_c	T_g	T_x	T_d	T_m
323	489	599	614	745

T_c Curie's, T_g glass transition, T_x crystallization, T_d decomposition and T_m melting temperatures respectively.
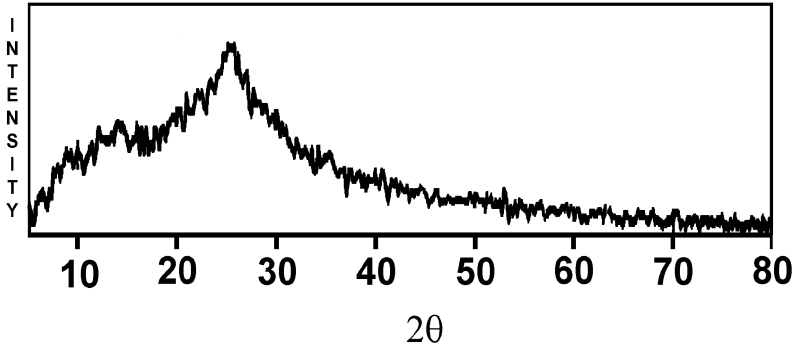
FIGURE 2 Cu K_α X-ray diffraction of PPANI.

3.2. Electron Microscope and X-ray Diffraction Analysis

Amorphous-like X-ray diffraction pattern is shown in Figure 2, small sharp diffraction lines may be due to minute amount of nanocrystalline precipitation with a glassy matrix. While the SEM electron microscopic micrograph shows micro sized granules material with
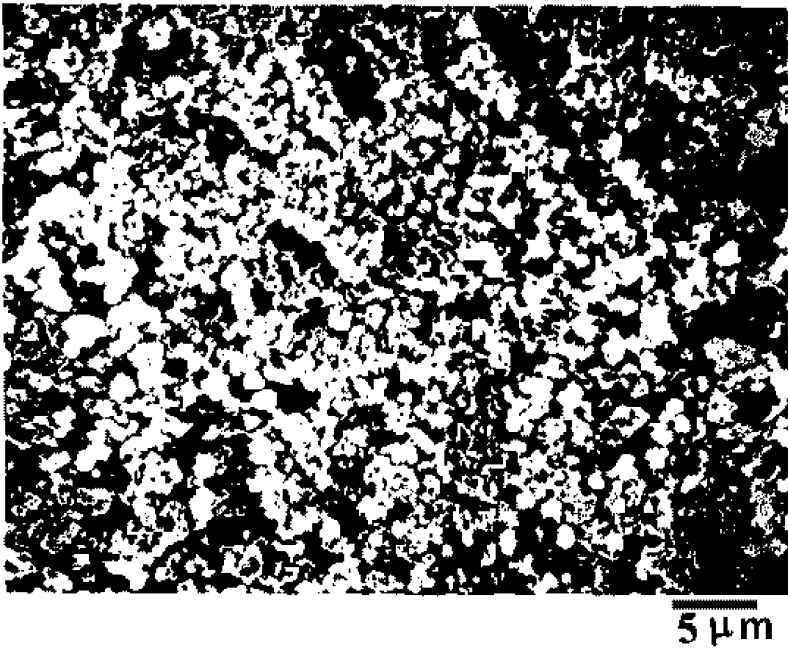

FIGURE 3 SEM of PPANI.

elongated shaped particles, as shown in Figure 3. Their particle size ranged from 1 to 5 μm.

3.3. Electrical Properties of Polyaniline

While attempts were conducted to study the d.c. electrical conductivity as a function of temperature for the PPANI it was noticed that a stimulated current persist at zero applied electric field. This phenomenon is due to pyroelectric effects. Consequently, short-circuit d.c. electrical measurement of this thermally stimulated current was measured as a function of temperature. As can be seen from Figure 4 a peak is observed with a maximum at 324 K (51°C). This observation pointed out that our PPANI sample might show ferroelectric behaviour below this temperature and accordingly may have interesting dielectric properties.

In order to clarify this observation further exploratory measurements were done. Measurements of dielectric constant and
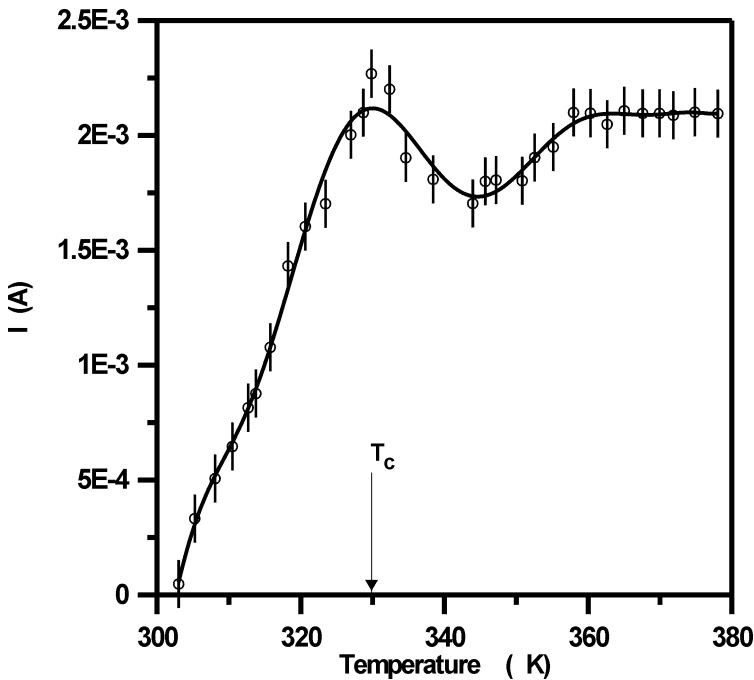

FIGURE 4 Pyroelectric current as a function of temperature of PPANI, showing a peak maximum at Curie's temperature T_c.

conductivity as a function of temperature and frequency are shown in Figure 5. Room temperature hysteresis loop on the other hand is shown in Figure 6 as an example. Polarization as a function of electric field strength (P-E) was traced as a function of applied field at room
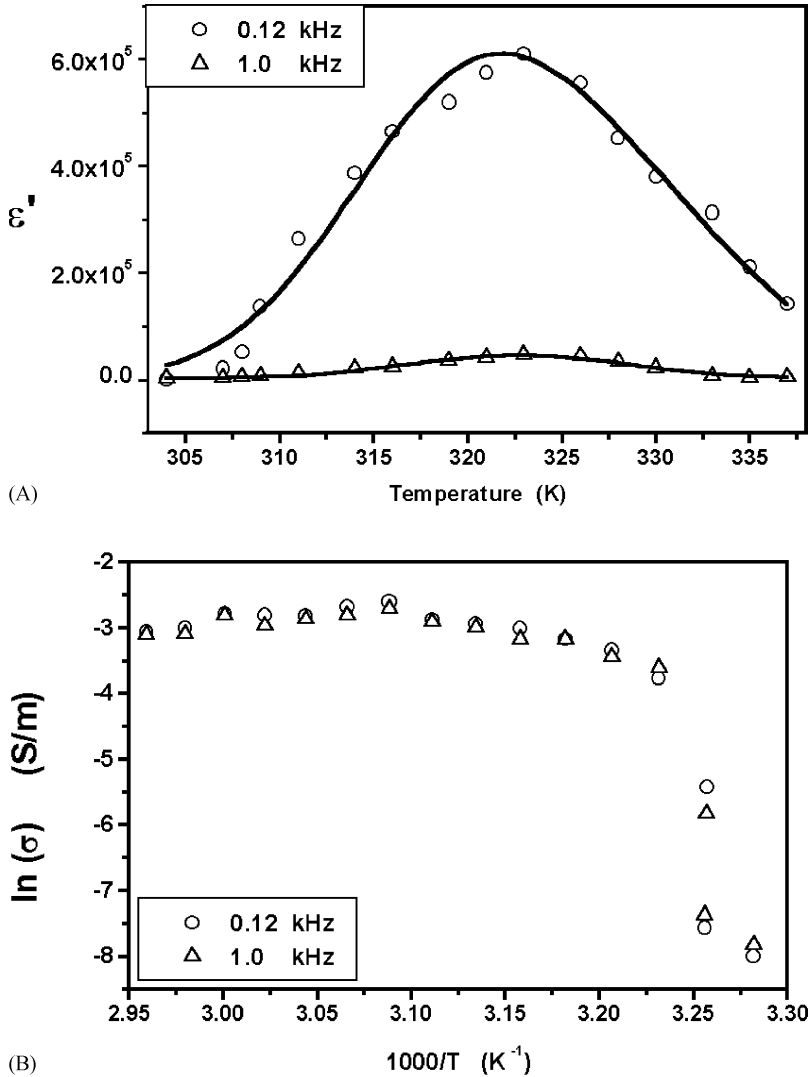
FIGURE 5 AC electrical properties at two different applied frequencies, 0.12 and 1.0 kHz, as a function of temperature. (A) dielectric constant and (B) electrical conductivity.
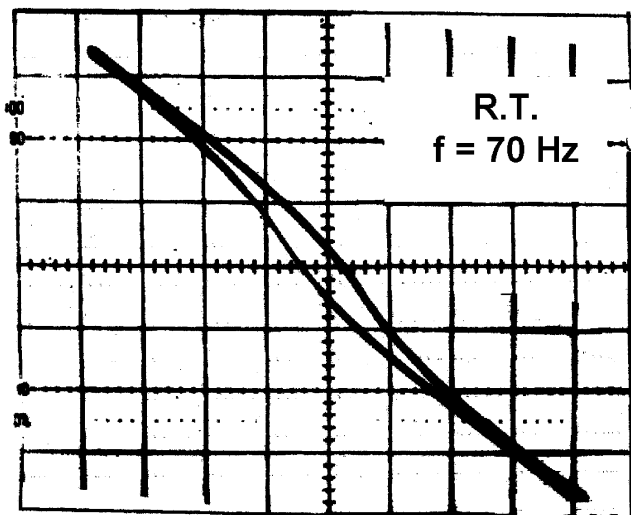
FIGURE 6 Representative hysteresis (E-P) loop at room temperature, E = 2 kV/cm and f = 70 Hz.

temperature and is shown in Figure 7. The temperature dependence of polarization at a constant applied field and frequency of 70 Hz is given in Figure 8.

DISCUSSION

The real part of the dielectric constant (ε') investigated as a function of temperature and frequency, Figure 5A, shows a peak with maximum at $T_c = 324$ K (51°C). Also the temperature corresponding to the peak maximum is found to be frequency independent while it become sharper at lower frequencies. Indicating that this dielectric dispersion is not due to Debye relaxation. Nearly at the same transition point (T_c) a sharp increase in the a.c. conductivity is observed as shown in Figure 5B, which may be due to a rapid increase in ions mobility. The conductivity also shows a frequency independent behaviour with a metallic like habit. The high permittivity value ($\sim 7.1 \times 10^5$) at the peak may be due to the presence of small amounts of protonation within the insulating region of the polymer which has only limited short range order. This result may be explained as due to freezing of ferroelectric fluctuations. Frustration between dipoles in the two states (nanocrystals − glass composite) is suggested to be a mechanism of the observed dielectric dispersion [43].
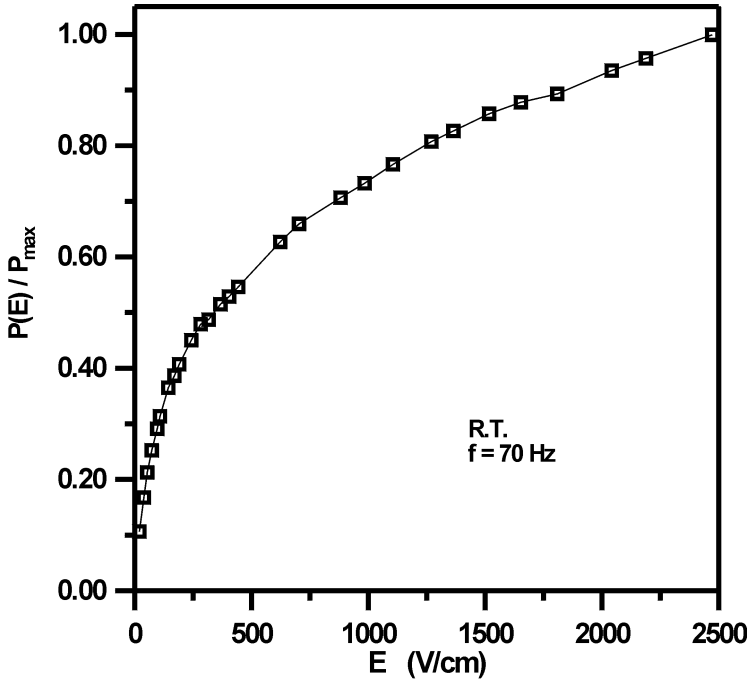
FIGURE 7 Room temperature reduced polarization of PPANI as a function of applied field (E-P).

Above the peak maximum, T_m, of the dielectric dispersion, ferroelectricity may be confirmed if the Curie's law applies [33];

$$\varepsilon = \frac{C}{T - T_o} \qquad (1)$$

a plot of the inverse $(1/\varepsilon)$ of the dielectric constant at $f = 0.12$ kHz as a function of temperature is shown in Figure 9. The obtained data according to Eq. (1) are: Curie's constant, $C = 3.92 \times 10^6$ K^{-1} , temperature at minimum $T_m(K) = 324$ K and an asymptotic Curie temperature, $T_o = 320.5$ K. From the figures and the above data it is clear that up to 340 K, the following observations could be out lined. Firstly, Curie's law is satisfied above T_c, which is accordingly may be assigned as the Curie's temperature. On the other hand Figure 9 shows that neither first nor second order transitions could be assigned to our dielectric data, where the ratio of the theoretical slopes below and
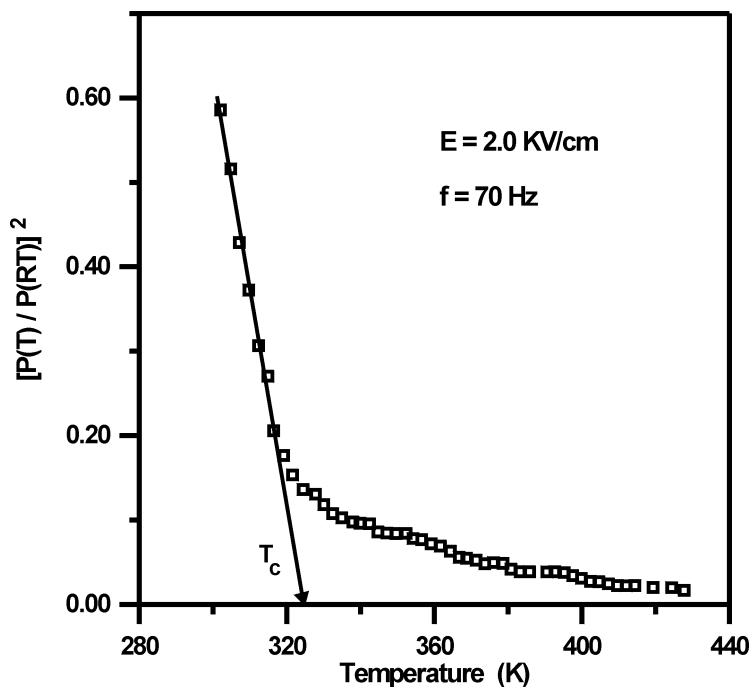
FIGURE 8 Square reduced polarization as a function of temperature according to Eq. (2), showing the Curie's temperature T_c.

above T_c should be -2 for a second order and about -4 or less for a first order transition [33]. This result could be explained as due to the successive degradation of the polymer as the temperature is increased (*cf.* Figure 1A), or due thermal diffuse phase transition DPT. Even so the DTA measurements support a first order phase transition by observing the first endothermic peak explained above.

The effect of temperature on the dielectric constant presented in Figure 5A and the corresponding Curie's plot in Figure 9 show a characteristic peak with dielectric constant approaching several thousands. This type of dispersion is a primary indication of ferroelectric behaviour below the peak maximum. The behaviour is irreversible only if the PPANI sample was heated to 380 K or above, where the dielectric constant do not show any more peaks on cooling down to room temperature, or if the preheated sample is subjected to a new set of dielectric measurements. The electrical conductivity on the other
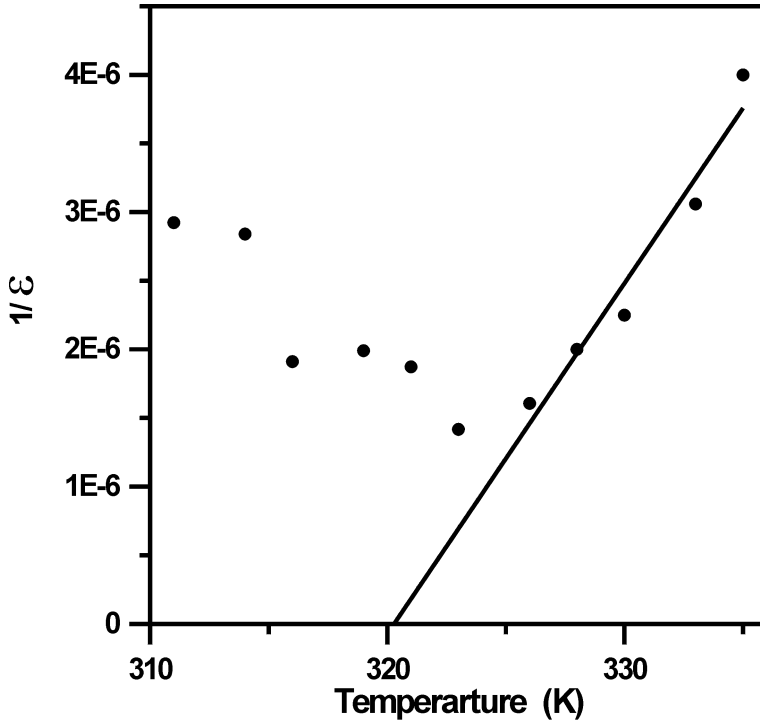
FIGURE 9 Curie's plot according to Eq. (1), showing the asymptotic Curie's temperature T_o.

hand shows a constant metallic like behaviour above 315 K, with almost a constant resistivity of 12.2 ohm m see Figure 5.

The predicted ferroelectric behaviour is confirmed next by applying four more different experimental verifications.

First, by studying the pyroelectric current as a function of temperature. This was done as given above in the temperature range $300-400$ K and the obtained data are graphically represented in Figure 4. It is noticed that the pyroelectric current is exceptionally high, reaching 2.1 mA and peaked at 324 K. The pyroelectric current peak occurred at the same temperature T_c observed in the dielectric measurements. Confirming two properties of ferroelectricity with two different independent experimental setups.

Second, ferroelectricity of the present PPANI was confirmed by observing the ferroelectric hysteresis loop as present for example in Figure 6 using the Sawyer Tower [34] instrumental setup.

Third, by studying the (P-E) hysteresis loop properties, such as the reduced polarization as a function of applied field at room temperature the familiar behaviour of ferroelectric P-E curve was obtained, as shown in Figure 7.

Fourth, by tracing the saturation polarization as a function of temperature the next known relation was confirmed to apply [35]:

$$\frac{P(T)}{P(RT)} = \left[\frac{T_c - T}{T_c}\right]^{1/2} \tag{2}$$

Figure 8 shows a decrease followed by a an inflection point at 324 K. The linear curve indicate the applicability of Eq. (2) to our experimental data. The intersecting point of the straight curve with the temperature axis represents the Curie's temperature, which is the same temperature obtained also from independent DTA, dielectric and pyroelectric measurements presented above. The above results indicate that the present PPANI sample shows ferroelectric behaviour below 324 K, while it is a paraelectric up to 340 K. Further heating cause successive degradation of the PPANI, and the ferroelectric behaviour disappears on cooling the sample to room temperature. This may be explained as due to dehydration and loss of water molecules (4-H_2O) of the polymer structure [30−32] as shown from the DAT and TG results.

The origin of the observed ferroelectricity can be interpreted with reference to the X-ray diffraction results that indicate that the sample may be a glassy/nanocrystalline composite, where the ferroelectric properties are determined by the interaction of polar nanocrystalites with charges in the glassy phase. Amorphous dielectric dispersion or ferroelectricity was observed on splat cooling, thin films, ball milled nanocrystalline powder, sol-gel [35−39] and in dipolar-glass system of $Rb_{1-x}(NH_4)_xH_2PO_4$ [40].

Ferroelectricity for materials in the amorphous state is considered to be a recent subject of interest. Where for example in recent years, Zhang and Widom [41] proposed a mean field theory that predicts ferroelectric phases in dipolar systems that lacked any specific spatial correlations, provided the density of the particles was above a critical value. They considered an amorphous solid of dipolar hard spheres where the particles were free to rotate, but were frozen at random sites. Their prediction of ferroelectric phases in dipolar systems that lack any specific spatial correlations suggests that well-tuned short-range structure may not be necessary for ferroelectric phase formation. They suggested that the experimental dipole density was possibly too low for ferroelectric order, and hence a dipolar glass state was

found. While at high densities, in contrast, the mean field dominates and ordering is possible and ferroelectricity may be observed above a critical density. Furthermore ferroelectricity was recently reported in a glassy material of composition $Bi_{1.8}$ $Pb_{0.3}$ Sr_2 Ca_2 $Cu_{2.8}$ $K_{0.2}$ O_y without any ambiguity [44].

However ferroelectrics with diffuse phase transition (DPT) such as ours are usually explained by the presence of dipole inhomogenty [42]. The inhomogenity is either ascribed to the composition fluctuation, which is almost macroscopic in scale, or to the fluctuation in chemical ordering, which is intermediate in length scale, or to glassy dipolar frustration of the macroscopic, ferroelectric, ordering of ions whose scale is of the order of lattice.

These results indicate that the polymer under study may be composed of nanocrystalline grains embedded in a glassy matrix. Similar results were observed in organic copolymers of polvinylidenefluoride (PVDF) with trifluroethylene [43] and in solid solutions of dipolar glass system $C_5NH_6BF_4/C_5NH_6PF_6$ [40].

According to the above discussion, it is clear that the investigated polyaniline behaves as an inorganic ferroelectric material below 323 K. This phenomenon is found to disappear if the PPANI sample was preheated above 380 K. The existence of the present phenomenon is obviously due to the preparation procedure undertaken in the present work.

REFERENCES

[1] Kalaji, M., Peter, L. M., Abrantes, L. M. and Mesquita, J. C. (1989). *J. Electroanal. Chem.*, **274**, 289.

[2] Lacroix, J. C., Kanazawa, K. K. and Diaz, A. (1989). *J. Electrochem. Soc.*, **130**, 1308.

[3] MacDiarmid, A. G., Chiang, J. C., Halpern, M., Huang, W. S., Mu, S. L., Somasiri, N. L. D., Wu, W. and Yaniger, S. I. (1985). *Mol. Cryst. Liq. Cryst.*, **121**, 173.

[4] MacDiarmid, A. G., Chiang, J. C., Richter, A. F. and Epstein, A. J. (1987). *Synth. Met.*, **18**, 285.

[5] MacDiarmid, A. G. and Epstein, A. J. (1989). *Faraday Discuss Chem. Soc.*, **88**, 317.

[6] Travers, T. V., Genoud, F., Menardo, C. and Nechtschein, M. (1990). *Synth. Met.*, **35**, 159.

[7] Miller, J. (1993). *Adv. Mater.*, **5**(8), 587ff and 671ff.

[8] Sakkopoulos, S., Vitoratos, E., Dalas, E., Pandis, G. and Tsamouras, D. (1992). *J. Phys.: Condens. Matter*, **4**, 2231.

[9] Dunsch, L. (1975). *J. Electroanal. Chem.*, **61**, 61.

[10] Sasalci, K., Kaya, M., Yano, J., Kitani, A. and Kunai, A. (1986). *J. Electroanal. Chem.*, **215**, 401.

[11] Genies, E. M. and Tsintavis, C. (1985). *J. Electroanal. Chem.*, **195**, 109.

[12] Shim, Y. B., Won, M. S. and Park, S. M. (1990). *J. Electrochem. Soc.*, **137**, 538.

[13] Wei, Y., Tong, X. and Sun, Y. (1989). *J. Poly. Sci. (A)*, *Polym. Chem.*, **27**, 2385.

[14] Wei, Y., Jang, G. W., Chan, C. C., Hsueh, K. F, Hariharan, R., Patel, S. A. and Whitecar, C. K. (1990). *J. Phys. Chem.*, **94**, 7716.

[15] Wei, Y., Sun, Y. and Tang, X. (1989). *J. Phys. Chem.*, **93**, 4878.

[16] Zotti, G., Cattarin, S. and Comisso, N. (1988). *J. Electroanaly. Chem.*, **239**, 387.

[17] Shim, Y. B. and Park, S. M. (1988). *Synth. Met.*, **29 E**, 169.

[18] Kogan, Ya. L., Davidova, O. L., Knerelman, E. L., Gedrovich, G. V., Fokeeva, L. S., Emelina, L. V. and Savchenko, V. L. (1991). *Synth. Met.*, **41−43**, 887.

[19] Roichan, Y. *et al.* (1999). *Synth. Metal*, **98**(3), 201.

[20] Aleshin, A. N., Lee Kwanghee, Lee, J. Y., Kim, D. Y. and Kim, C. Y. (1999). *Synth. Met.*, **99**, 27.

[21] Joo, J., Song, H. G., Jeong, C. K., Baeck, J. S., Lee, I. K. and Ryu, K. S. (1999). *Synth. Met.*, **98**, 215.

[22] Armes, S. P. and Milhier, J. F. (1988). *Synth. Met.*, **22**, 385.

[23] Armes, S. P. and Aldissi, M. (1991). *Polymer*, **32**(11), 2043.

[24] Yoke Fong and Joseph B. Schlenoff (1995). *Polymer*, **36**(3), 639.

[25] Yong Gao, Suzhen Li, Zhijiann Xue and Ding Guo (1986). *Synth. Met.*, **16**, 305.

[26] Yong Gao, Akjandro Andreatta, Alan, Heeger, J. and Smith, P. (1989). *Polymer*, **30**, 2305.

[27] Show An Chem and Gue Wuu Hwang (1997). *Polymer*, **38**(11), 3333.

[28] Wang Shenglong, Wang Fosong and Ge Xiaohui (1986). *Synth. Met.*, **16**, 99.

[29] Zeng Xing Rong and Ko Tze Man (1998). *Polymer*, **39**(5), 1187.

[30] Sayyah, S. M., Abd El-Khalek, A. A., Bahgat, A. A. and Abd-ElSalam, H. M. (2001). *Polym. Int.*, **50**, 197.

[31] Sayyah, S. M., Abd El-Khalek, A. A., Bahgat, A. A. and Abd-ElSalam, H. M., *Int. J. Polym. Materials*, in press.

[32] Sayyah, S. M., Bahgat, A. A. and Abd-ElSalam, H. M., *Int. J. of Polym. Materials*, in press.

[33] Lines, M. E. and Glass, A. M., "Principles and Applications of Ferroelectrics and Related Materials", Clarendon Press, Oxford, 1977.

[34] Sawyer, C. B. and Tower, C. H. (1930). *Phys. Rev.*, **35**, 269.

[35] Lines, M. E. (1977). *Phys. Rev. B*, **15**, 388.

[36] Glass, A. M., Lines, M. E., Nassau, K. and Shiever, J. W. (1977). *Appl. Phys. Lett.*, **31**, 249.

[37] Kui Yao, Weiguang Zhu, Liangying Zhang and Xi Yao (1997). *Jpn. J. Appl. Phys.*, **36**, 4369.

[38] MacKenzie, J. D., Xu, R. and Xu, Y., *US patent No. US5342648*, *Issued/Filed Dates*: Aug. 30, 1994/Sept. 23, 1992.

[39] Shantha, K. and Varma, K. B. R. (1999). *Matr. Sci. and Engin.*, **B56**, 66.

[40] Hanaya, M., Nomoto, M., Miura, T. and Oguni, M. (2000). *Solid State Communications*, **115**(2), 57.

[41] Zhang, H. and Widom, M. (1995). *Phys. Rev.*, **B51**, 8951.

[42] Woong Kil Choo and Hyo Jin Kim (1992). *J. Phys.*: *Condens. Matter*, **4**, 2309.

[43] Ploss, B. and Ploss, B. (1996). *Ferroelectrics*, **184**, 107.

[44] Bahgat, A. A. and Kamel, T. M. (2001). *Phys. Rev.*, **B63**(1), 01201.