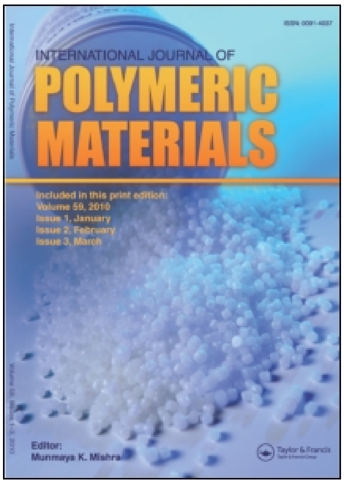

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Influence of Low Energy Ar Ion Beam and UV-Irradiation on A.C. Electrical Conductivity of Polyacrylonitrile

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The influence of low energy Ar^+ ion beam and UV-irradiation on polyacrylonitrile (PAN) polymer was investigated using a.c. electrical conductivity. A.c. electrical conductivity of PAN was measured at the frequency range of 2×10^2–5×10^6 Hz and temperature range of 303–473 K. The experimental results indicate that the a.c. conductivity depends on the frequency and temperature for unirradiated and irradiated PAN samples. It shows that the influence of low energy Ar^+ ion beam on PAN is more effective compared with UV-radiation. It was found that at frequencies above 2×10^4 Hz all samples follow a power low of the frequency, $\sigma_{ac}(\omega) \propto \omega^S$. The frequency exponent S is dependent on the temperature. The conduction mechanism is reasonably well interpreted in terms of the correlated barrier hopping (CBH) model.

Keywords: polymer, polyacrylonitrile, a.c. conductivity, influence of ion beam, UV-irradiation

INTRODUCTION

The radiation chemistry of polymers has become of great interest in recent times [1,2]. Ionizing radiation may induce several changes in structure of polymers, bond, and chain scission, changes in gas adsorption, crystallinity, and un-saturation being the main effects. Modification of polymer properties by radiation can be used in industry in

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the production of heat shrinkable films and tubing, crosslinked polymers and graft copolymers [3]. The short exposure of a polymer to ions of inert or reactive gases leads to the formation of a crosslinked surface layer of a high cohesive strength. Such polymers are ideal for the production of strong adhesive joints [4]. Crosslinking occurs when two free dangling ions or radical pairs on neighboring chains unite, whereas double or triple bonds are formed if two neighboring radicals in the same chain unite. It has been well established that mechanical, physical, and chemical properties changes in polymers are determined by the magnitude of crosslinking and scission [5]. Electrical conductivity increases due to the formation of crosslinks and conjugated double and triple bond by irradiation [6]. The induced degradation by low energy of Ar^+ ion beam and UV radiation of ployacrylonitrile (PAN) was investigated [7–10]. PAN is a semi-crystalline vinylic homopolymer with repeating unit $-(CH_2-CHCN)-$, usually in atactic form [11]. The surface of the polymer has been successfully modified by a combination of low energy ion beam and reactive gas environment [12–16].

The d.c. electrical properties of PAN material have been studied [7]. As an extension to that work, the study of a.c. conductivity will be the main objective. In the present investigation, the influence of low energy Ar^+ ion beam and UV-irradiation on Polyacrylonitrile (PAN) as thin discs was investigated using a.c. electrical conductivity. It was measured at different frequencies and temperatures for different irradiation times, t_{exp}.

EXPERIMENTAL ARRANGEMENT

Synthesis of Polymers

Using $K_2S_2O_8$ as initiator in water solvent for 3 h, Polyacrylonitrile (PAN) was prepared by homopolymerization of acrylonitrile. The polymer was dried at 313 K for several hours. PAN powder were pressed under pressure of 10 ton/cm^2 into small discs of diameter 1.3 cm using evacuated press.

Ion Beam Irradiation Arrangement

The low energy Ar^+ ion beam irradiation was carried out using a glow discharge ion source [15], enabling the irradiation of the polymer samples with a low energy (mean value 1 keV), high density (8 mA/cm^2), and focused ion beam with a divergence half angle of 5°. In order to have the ion source in a fixed position inside the chamber, a rig to carry the source and ion beam diagnostic system was designed. This ensured that the center of the ion beam exit hole was horizontal, which is necessary for ion beam irradiation processes. The samples were irradiated at nearly normal incidence with low energy argon Ar$^+$ ion beam for different irradiation times ($t_{exp} = 1$, 2, and 8 h).

UV-irradiation

The PAN discs were irradiation at room temperature in air with a full spectrum sodium lamp (Phillips – G/5812 So N), 500 watt, at a distance of 20 cm for different irradiation times ($t_{exp} = 8$ and 16 h).

A.C. Conductivity Measurements

The polyacrylonitrile (PAN) samples were covered on both sides with thin layer of a silver paste to obtain good contact and were mounted between two brass electrodes in a special holder. Then the sample holder was inserted in a small furnace and the temperature was measured to better than ±1°C with calibrated Ni–NiCr thermocouple, which was set up near the sample. The total a.c. conductivity $\sigma_t(\omega)$ of PAN samples was calculated from the measured value of the impedance Z using Hioki 3532 LCR meter. The total a.c. conductivity was calculated from the equation:

$$\sigma_t(\omega) = d/ZA \tag{1}$$

where d is the sample thickness and A is the cross sectional area of the sample.

The measurements were carried out in the frequency range of 2×10^2–5×10^6 Hz within a controlled temperature range of 303–473 K.

RESULTS AND DISCUSSION

Frequency and Temperature Dependence of the a.c. Conductivity

The total measured conductivity $\sigma_t(\omega)$, is related to the d.c. conductivity σ_{dc} and the component $\sigma_{ac}(\omega)$ of the conductivity by the relationship:

$$\sigma_{ac}(\omega) = \sigma_t(\omega) - \sigma_{dc} \tag{2}$$

where σ_{dc} is the d.c. conductivity measured previsouly [7].

Unirradiated PAN Sample

Figure 1 shows the a.c. conductivity ln $\sigma_{ac}(\omega)$ as a function of the reciprocal temperature at different frequencies in the range of 2×10^2–5×10^6 Hz for unirradiated PAN sample. The a.c. conductivity in Figure 1 shows a low temperature dependence with increasing frequency, but it increases at higher temperature. It has the same behavior at constant temperature with increasing frequency. It is clear that the a.c. conductivity increases with the temperature, and the slope of the tangent for each relation has a larger value at higher temperature. It is obvious at the low frequency range. A feature common to almost all amorphous semiconductors, polymers, and some other disordered systems, is that the a.c. conductivity, $\sigma_{ac}(\omega)$, increases with increasing frequency, according to the power law relation:

$$\sigma_{ac}(\omega) = A\,\omega^{s} \tag{3}$$

where A is a constant, ω is the angular frequency, and the frequency exponent S is ≤ 1.

The frequency dependence of $\sigma_{ac}(\omega)$ for unirradiated PAN samples at various temperatures is found to nicely follow Eq. 3. A typical set

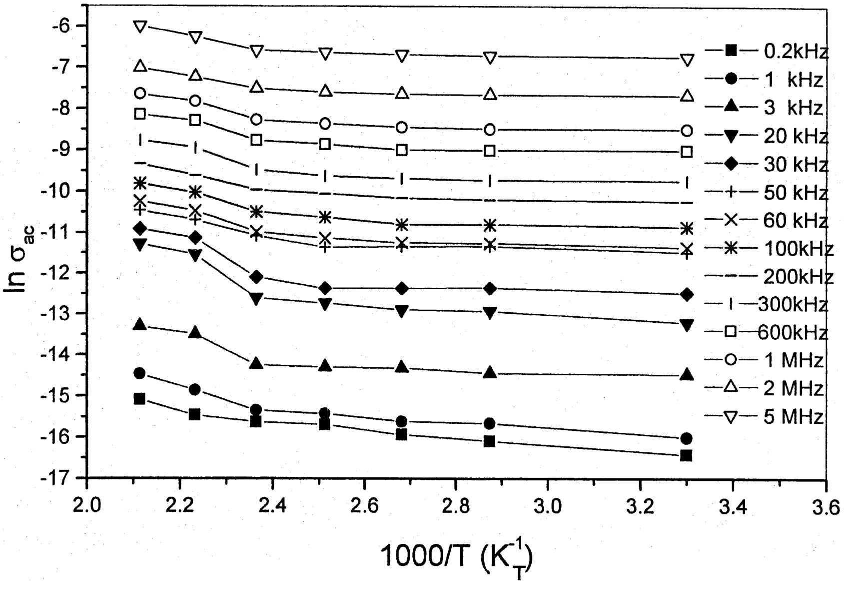

FIGURE 1 Variation of σ_{ac} with temperature T at different frequencies for unirradiated PAN sample.

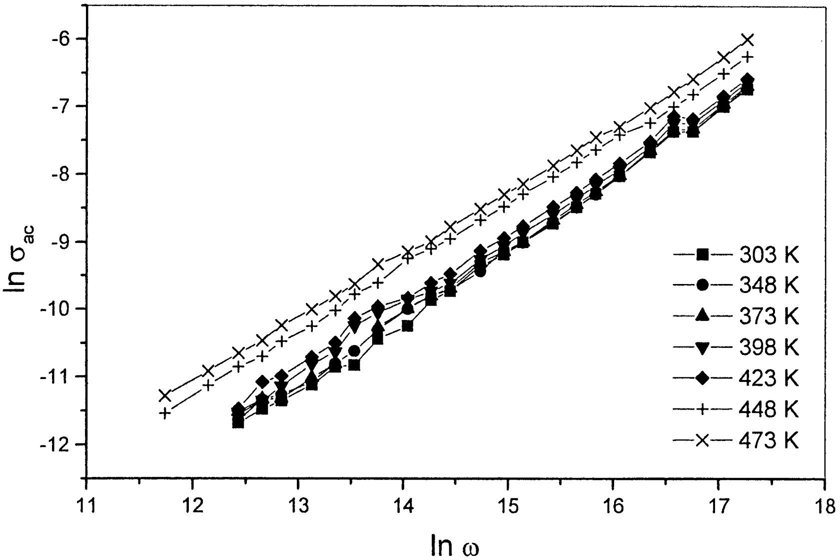

FIGURE 2 The a.c. conductivity dependence on the frequency at constant temperature for unirradiated PAN sample.

of plots of ln $\sigma_{ac}(\omega)$ against ln ω for unirradiated PAN samples shows a linearity in the range of 2×10^4–5×10^6 Hz in Figure 2. Furthermore, a nonlinearity of ln $\sigma_{ac}(\omega)$ against ln ω was observed below frequency 2×10^4 Hz and 6×10^4 Hz at temperature above and below 423 K, respectively. It is clear from the figure that $\sigma_{ac}(\omega)$ linearly increases with increasing frequency and temperature, which is most likely due to the hopping of two electrons between two pairs of localized states. The frequency exponent S calculated from the slopes of ln ω versus ln $\sigma_{ac}(\omega)$ graph for the temperature and frequency ranges is plotted as a function of temperature in Figure 3 for unirradiated sample. This figure shows a decrease in exponent $S \approx 1.043$ at 303 K with an increase of temperature to ≈ 0.943 at 473 K through the frequency and temperature ranges. Different models have been proposed to interpret the frequency and temperature dependence of a.c. conductivity in amorphous glasses and polymers materials. The first model is quantum mechanical tunneling (QMT) [17], which suggests that $\sigma_{ac}(\omega, T)$ should increase linearly with increasing temperature and the frequency exponent S is almost equal to 0.8 and increases slightly with increasing temperature or independent of temperature. Therefore QMT model is not applicable to the obtained results.

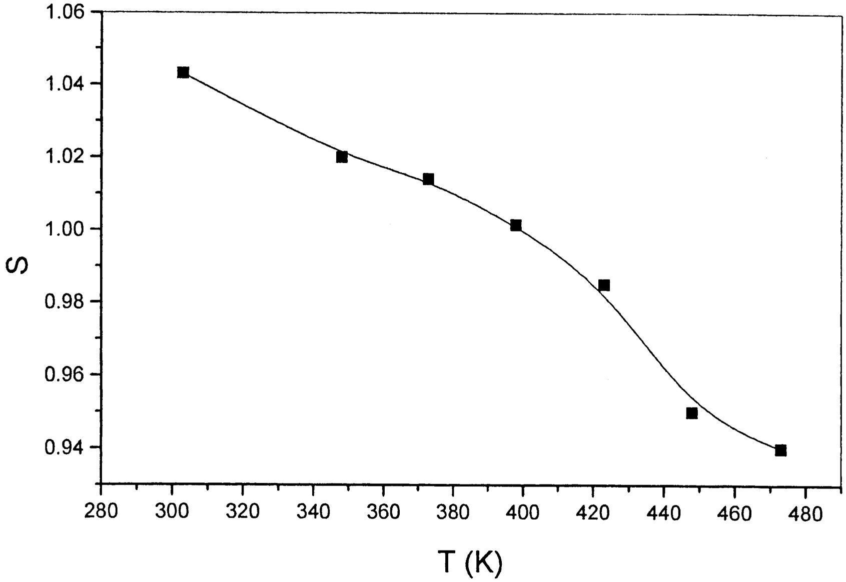

FIGURE 3 The temperature dependence of the frequency exponent S for the unirradiated PAN sample.

The second is the overlapping–large polaron tunneling (OLPT) model [18]; the exponent S is both temperature and frequency dependent. S decreases with increasing temperature from unity at room temperature to a minimum value at a certain temperature and then it increases with increasing temperature. Therefore, OLPT model is also not applicable to the obtained results.

The third model is the correlated barrier hopping (CBH) one [19], where values of the frequency exponent S range from 0.7 to 1 at room temperature and decrease with increasing temperature. This is in good agreement with the obtained results of PAN samples, so the frequency dependence of $\sigma_{ac}(\omega)$ can be explained in terms of CBH model at frequencies higher than 2×10^4 Hz.

The resolution of $\sigma_t(\omega)$ into σ_{dc} and $\sigma_{ac}(\omega)$ has a fundamental significance, as σ_{dc} and $\sigma_{ac}(\omega)$ mostly arise from different processes in different states, because σ_{dc} is due to extended states and $\sigma_{ac}(\omega)$ is due to localized states [20]. The frequency dependence of hopping in localized states has been treated by many authors [19–23]. The shape of the curves in Figure 1 suggests two different regimes with different activation energies, one with weak temperature dependence and the other with strong temperature dependence.

TABLE 1 Activation Energies of PAN Polymer Sample Below the Temperature 423 K, Region I and Above the Temperature 423 K, Region II

Frequency F (kHz)	E_a (eV) Region 1	E_a (eV) Region 11
0.2	0.076	0.183
1	0.060	0.304
3	0.022	0.330
20	0.053	0.462
30	0.027	0.409
50	0.028	0.214
60	0.0211	0.207
100	0.031	0.239
200	0.025	0.218
300	0.021	0.244
600	0.010	0.170
1000	0.019	0.218
2000	0.013	0.171
5000	0.014	0.203

The a.c. conductivity $\sigma_{ac}(\omega)$ as a function of temperature at constant frequency is written in the form [24,25]:

$$\sigma_{ac}(\omega) = B\exp(-E_a/kT) \tag{4}$$

where B is constant, E_a the activation energy for conduction, and k is the Boltzmann constant. The values of E_a calculated from Eq. 4 is essentially dependent on the frequency. The activation energy E_a calculated, using the data in Figure 1 above and below the temperature 423 K are shown in Table 1. It is evident in this table that E_a above 5×10^4 Hz and 423 K is nearly constant with values of about 0.20 eV ± 0.03.

Effect of Low Energy Ar^+ Ion Beam

Measurements of a.c. conductivity in low energy Ar^+ ion beam irradiated PAN samples have been carried out at the frequency range of 2×10^2–5×10^6 Hz and the temperature range of 303–473 K with different irradiation times ($t_{exp} = 1$, 2, and 8 h). Figure 4 shows the relation between ln $\sigma_{ac}(\omega)$ and 1000/T at constant frequency of 6×10^4 Hz, as an example, before and after irradiation of the samples. From this Figure, it is clear that the a.c. conductivity $\sigma_{ac}(\omega)$ increases by increasing t_{exp}. Also, as in unirradiated samples, there are two regimes in the conductivity by increasing the temperatures. The value of the conductivity increases concomitantly with increasing Ar^+ ion beam irradiation time.

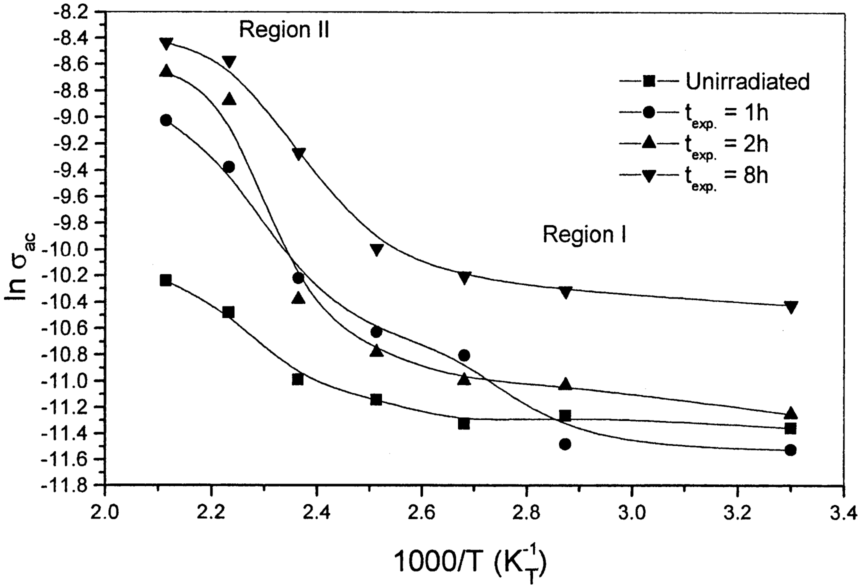

FIGURE 4 Variation of $\sigma_{ac}(\omega)$ with temperature T at the frequency $F = 6 \times 10^4$ Hz with different Ar^+ ion beam irradiation times for PAN samples.

Ion irradiation of polymers generates a number of charged species such as free radicals, ions, and other low molecular weight charged species, and so on, and the mobility of these species contributes to the conductivity.

On the other hand, the increase in the conductivity generally has been attributed to an increase in the mobility of these molecular charged species due to a decrease in the degree of the crystallinity [26,27].

Table 2 illustrates the activation energy E_a of Ar^+ ion beam irradiated PAN samples, calculated using the data measured above the temperature 398 K (in region II) at different t_{exp} (1, 2, and 8 h). It is evident that E_a is nearly constant above the frequency 5×10^4 Hz. Also, at the temperature below 398 K and the frequency 5×10^6 Hz as an example, E_a is low in three samples, equaling 0.043, 0.039, and 0.031 eV for $t_{exp} = 1$, 2, and 8 h, respectively.

Figure 5a and b shows that $\ln \sigma_{ac}(\omega)$ increases linearly with increasing $\ln \omega$ in the frequency ranges of 5×10^4–5×10^6 Hz at 303 K and of 8×10^3–5×10^6 Hz at 473 K for unirradiated and low energy Ar^+ ion beam irradiated samples. Here it follows the relation (3). The frequency exponent S was calculated for different Ar^+ ion beam irradiation times

TABLE 2 Activation Energies of PAN Polymer Sample Above the Temperature 398 K, Region II for Different Irradiation Times of Low Energy Ar$^+$ Ion Beam

Frequency F (kHz)	E_a (eV) 1 h	E_a (eV) 2 h	E_a (eV) 8 h
0.2	0.633	0.812	0.078
1	—	0.644	0.232
3	0.284	0.999	0.283
20	0.533	0.522	0.440
30	0.627	0.532	0.306
50	—	0.567	0.306
60	0.415	0.600	0.352
100	0.477	0.600	0.366
200	0.473	0.568	0.335
300	0.439	0.584	0.349
600	0.477	0.601	0.337
1000	0.496	0.610	0.331
2000	0.454	0.603	0.301
5000	0.501	0.583	0.262

using the slope of the data of ln $\sigma_{ac}(\omega)$ versus ln ω and plotted as function of temperature in Figure 6. It is clear from this figure that the frequency dependence of $\sigma_{ac}(\omega)$ can be also explained in terms of CBH model above the 5×10^4 Hz frequency.

Effect of UV-Irradiation

The a.c. conductivity of irradiated PAN samples were studied in the frequency range of 2×10^2–5×10^6 Hz and temperature range of 303–473 K for different UV-irradiation times ($t_{exp} = 8$ and 16 h). Figure 7 shows the ln $\sigma_{ac}(\omega)$ dependence on reciprocal temperature at constant frequency $= 6 \times 10^4$ Hz, as an example, for PAN before and after UV-irradiation with different irradiation times. It is clear from this figure that the conductivity decreases at UV-irradiation time 8 h. The decrease in the conductivity may be attributed to the creation of trapping centers [28]. On the other hand, the short exposure of a UV-irradiation leads to the formation of crosslinked surface layer of a high cohesive strength [29]. The increase in the a.c. conductivity with increased irradiating time of 16 h may be attributed to the generation of charged species [26–27].

Table 3 illustrated the activation energy E_a of UV-irradiated PAN samples, calculated using the data measured above the temperature 423 K (in region II) at different t_{exp} (8 and 16 h). It is evident that E_a is nearly constant above the frequency of 5×10^4 Hz. Also at the

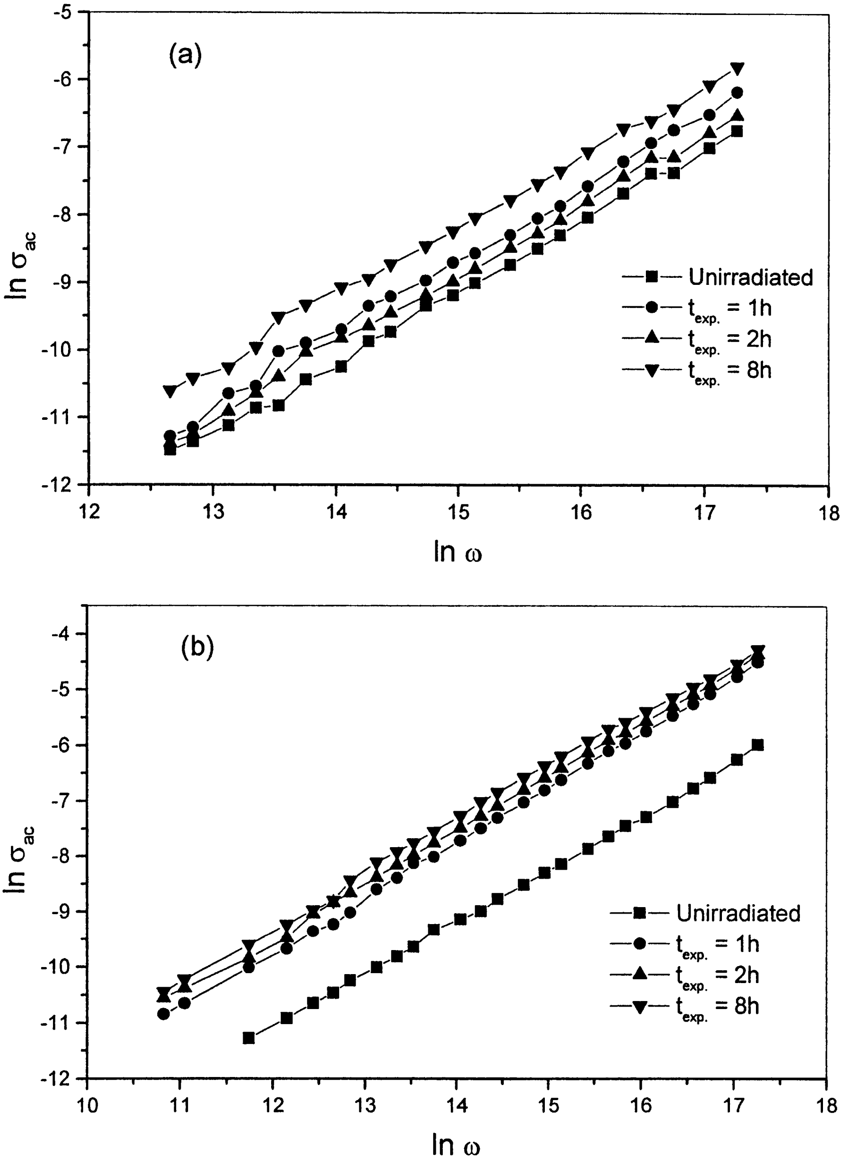

FIGURE 5 The a.c. conductivity dependence on the frequency for PAN before and after Ar^+ ion beam irradiation at (a) 303 K and (b) 473 K.

temperature below 423 K and the frequency 5×10^6 Hz, as an example, E_a is low in two samples and is 0.0005 and 0.014 eV for $t_{exp} = 8$ and 16 h, respectively.

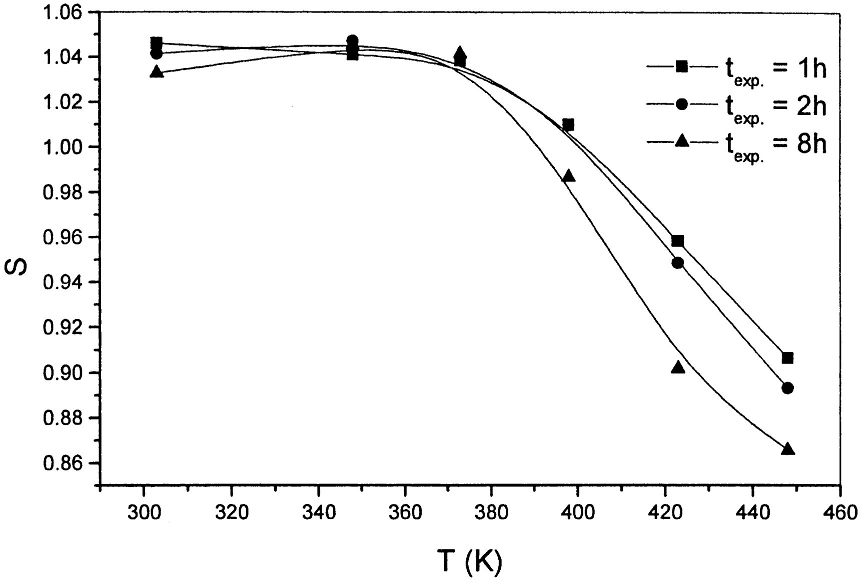

FIGURE 6 The temperature dependence of the frequency exponent S at different Ar^+ ion beam irradiation times for PAN samples.

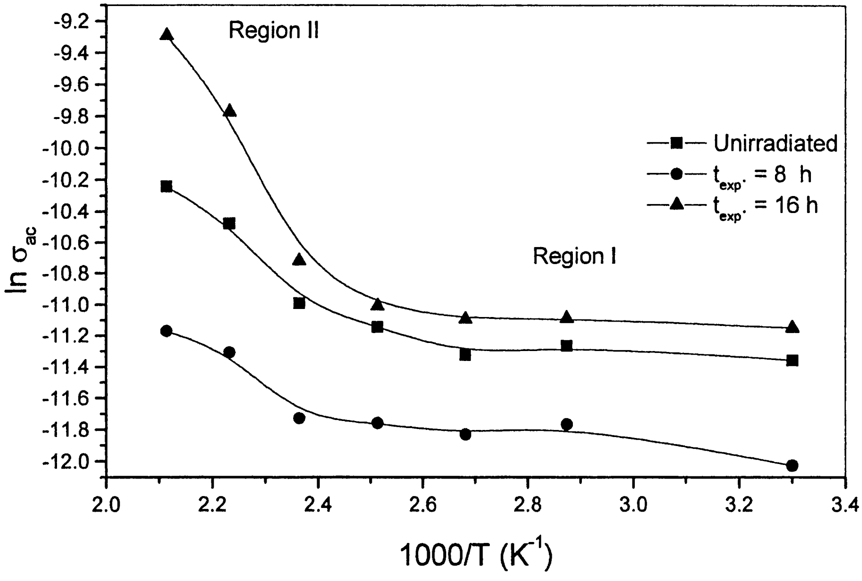

FIGURE 7 Variation of $\sigma_{ac}(\omega)$ with temperature T at the frequency $F = 6 \times 10^4$ Hz with different UV-irradiation times for PAN samples.

TABLE 3 Activation Energies of PAN Polymer Sample Above the Temperature 423 K, region II for Different Times of UV-Irradiation

Frequency F (kHz)	E_a (eV) 8 h	E_a (eV) 16 h
0.2	0.022	0.285
1	0.120	0.454
3	0.048	0.513
20	0.195	0.546
30	0.243	0.624
50	0.115	0.522
60	0.194	0.495
100	0.117	0.553
200	0.139	0.522
300	0.118	0.575
600	0.133	0.544
1000	0.128	0.546
2000	0.091	0.466
5000	0.116	0.455

Figure 8a and b shows that $\ln \sigma_{ac}(\omega)$ increases linearly with increasing $\ln \omega$ of UV-irradiated PAN samples in the frequency ranges of 4×10^4–5×10^6 Hz at 303 K and of 2×10^4–5×10^6 Hz at 448 K for $t_{exp} = 8$ and 16 h. So, it follows the relation (3). The frequency exponent S was calculated for two samples and plotted with the temperature in Figure 9. It is clear from this figure that the frequency dependence of $\sigma_{ac}(\omega)$ can also be explained in terms of CBH model above the frequency 4×10^4 Hz. As a general rule, the values for E_a of more than 0.6 eV would normally be associated with ionic transport and values less than 0.2 eV should be considered as indicating an electronic mechanism [30,31].

CONCLUSION

In summary, the obtained results of frequency and temperature dependence of a.c. conductivity have been found to support the CBH model, where the frequency dependence of a.c. conductivity is linear at high frequencies, and the exponent S is temperature dependent, decreasing with increasing temperature through the temperature and frequency ranges for unirradiated, Ar^+ ion beam, and UV-irradiated PAN samples.

Low energy Ar^+ ion beams have proven to be more effective in modifying polymer conductivity than UV-irradiation. This is because energetic ions have much higher linear energy transfer than other irradiation types.

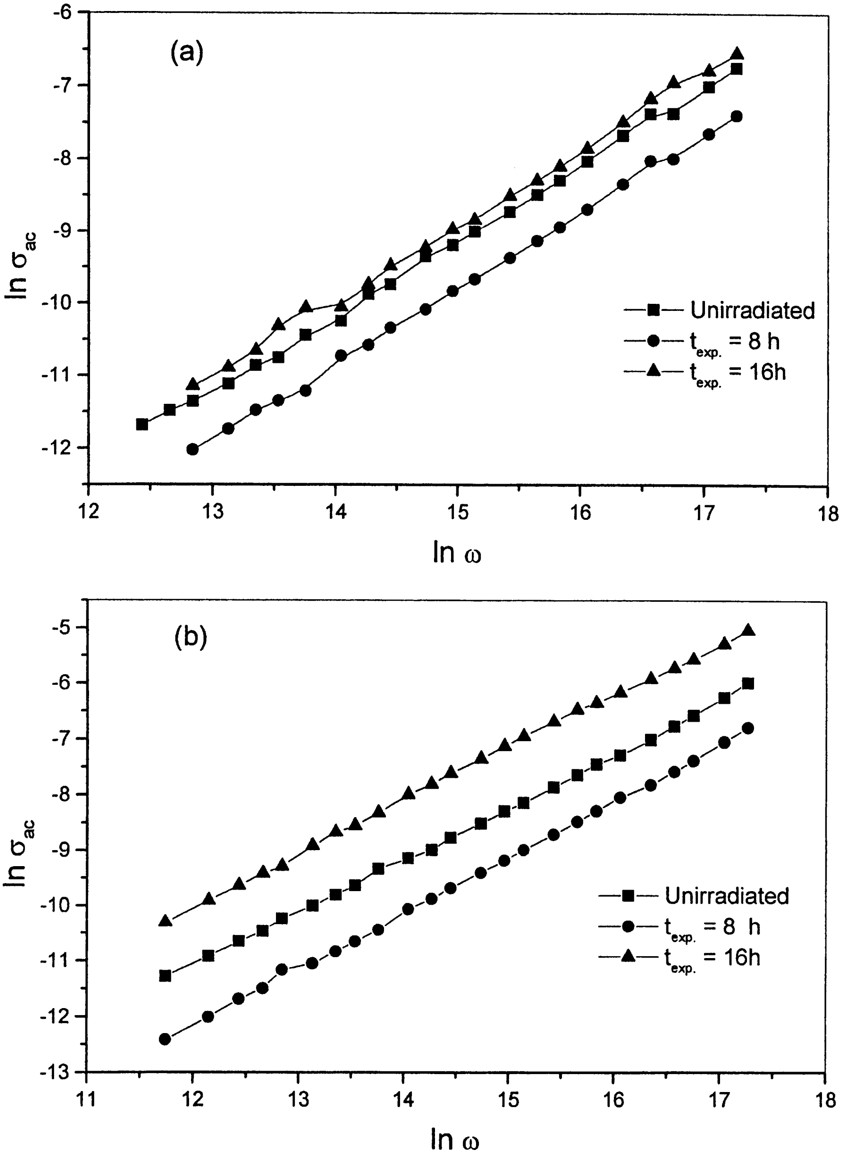

FIGURE 8 The a.c. conductivity dependence on the frequency for PAN before and after UV-irradiation at (a) 303 K and (b) 473 K.

The a.c. electrical conductivity measurements indicate that the conductivity increases after irradiation with Ar$^+$ ion beam and with UV for 16 h whereas it decreases after UV-irradiation for 8 h.

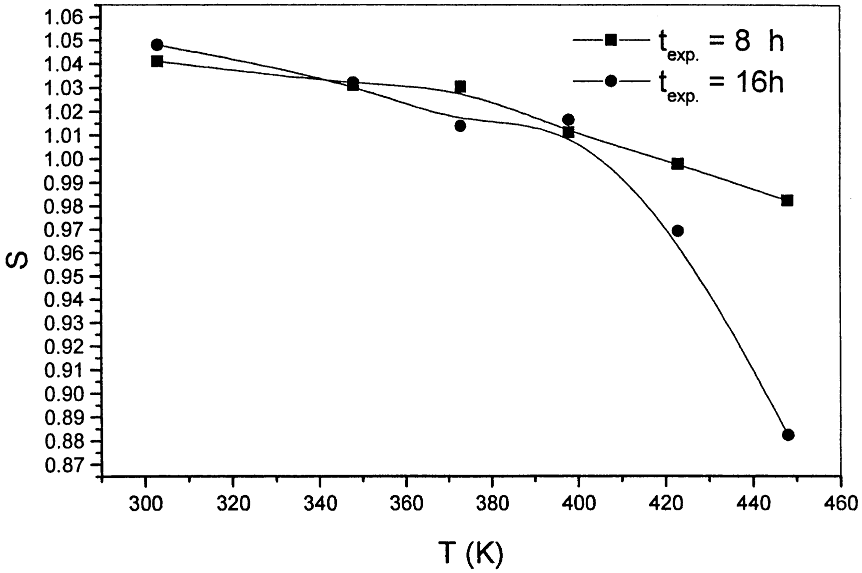

FIGURE 9 The temperature dependence of the frequency exponent S at different UV-irradiation times for PAN samples.

The calculated a.c. activation energies E_a, at low temperature demonstrate the minimal effect of Ar^+ ion beam and UV-irradiation. However at high temperatures E_a was nearly constant over frequency $>5 \times 10^4$, and increased by Ar^+ ion beam more than by UV-irradiation.

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