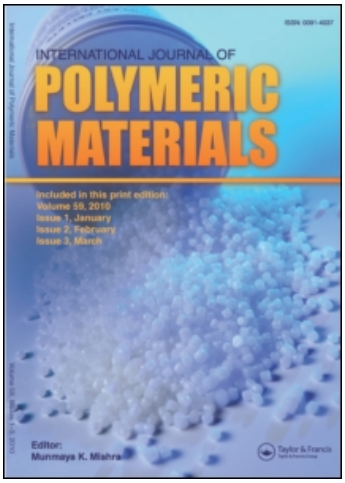

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Laser irradiation effect on the electrical properties of dyed poly vinyl alcohol (PVA)

M. A. Ahmed[a]; M. A. El-Ahdal[b]
[a] Physics Department, Cairo University, Giza, Egypt [b] Radiation Protection and Dosimetry Department, National Center for Radiation Research and Technology, Nasr City, Cairo, Egypt

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LASER IRRADIATION EFFECT ON THE ELECTRICAL PROPERTIES OF DYED POLY VINYL ALCOHOL (PVA)

M. A. Ahmed
Physics Department, Cairo University, Giza, Egypt

M. A. El-Ahdal
National Center for Radiation Research and Technology
Radiation Protection and Dosimetry Department
Nasr City, Cairo, Egypt

Dielectric spectroscopy of dyed poly (vinyl alcohol) irradiated with laser was investigated. The samples were irradiated with NdYAG laser source for 1, 2, 4 and 6 minutes. Dielectric constant and the electrical conductivity measurements are used to optimize the effect on the samples. Irradiation the samples for 1 minute and applying a frequency of 0.4 MHz at temperature 429 K represents the optimal conditions for our study.

Keywords: PVA; Laser; Electrical properties

INTRODUCTION

Recently many researchers have focused their work on polymer samples due to their wide range of applications especially in electronic devices. The discovery of highly stable polymers helps in such application. Rupturing of chemical bonding by irradiation yields free ions from these ones and at the same time the electrons and atoms are displaced and change the conduction mechanism. Moreover, the obtained free radicals can interact with each other and with the surrounding medium. The wide spread of laser applications in many branches of science paved the way for many investigations. Laser sources are either used to study the properties of some materials or to improve their behavior.

Semicrystalline poly (vinyl alcohol) (PVA) has a two-dimension hydrogen bonded network sheet structure. The sheets themselves are stacked and

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Address correspondence to M. A. Ahmed, Physics Department, Cairo University, Giza, Egypt.

bonded together by van der Waals forces. Modifications of this polymer alter its characteristic and its use. The use of dyes and transition metals to make composites and complexes with poly (vinyl alcohol) were meant to change its properties [1–4] to match new applications. PVA is a biocompatible polymer that has been used for the preparation of some hydrogels, and potentially used as a synthetic membrane or an interchange resin. The good strength, optical transparency, low permeability and solubility of poly (vinyl alcohol) made it to be the goal of an intensive study in the field of Laser fusion [5–7].

EXPERIMENTAL

Poly (vinyl alcohol) (PVA) polymer was dissolved in triply distilled water at 50°C using a magnetic stirrer for 24 hours. 3 mg of anilidine was dissolved in 5 ml absolute ethyl alcohol. The two solutions were mixed with each other. Pettri dish placed on levelled table was used for casting the polymer solution to obtain a uniform thickness sheet. The films were irradiated with laser beam from NdYAG source for 1, 2, 4 and 6 minutes.

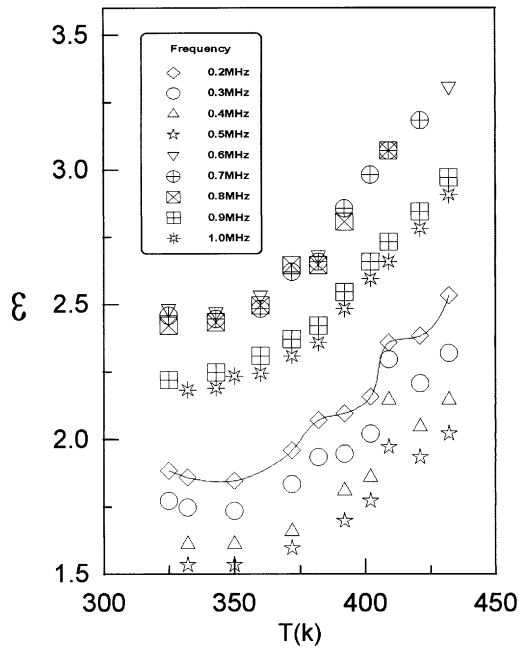

FIGURE 1 The dependance of the real part of the dielectric constant of unirradiated dyed PVA on temperature as function of frequency.

All samples used in the dielectric measurements were covered with silver paste (BDH) on both sides and checked for good contact. The sample was inserted between two metal electrodes. During heating runs, the sample temperature was raised by means of non-inductive cylindrical furnace operated a variable transformer. The temperature was measured using T-type thermocouple with junction just in contact with the sample. The accuracy of temperature measurement was better than $\pm 1°C$. Dielectric constant measurements as well as ac conductivity were achieved using a HIOKI 3530 RCL bridge (Japan).

RESULTS AND DISCUSSION

Figure 1 shows the dependence on temperature of the real part of dielectric constant (ε') of unirradiated dyed PVA as a function of frequency of the external applied electric field. For a certain frequency the dielectric constant increases with the temperature and shows three anomalies at temperatures 357, 385 and 409 K. The first pronounced anomaly is apparently due to the glass transition of the samples and the other temperatures may be related to

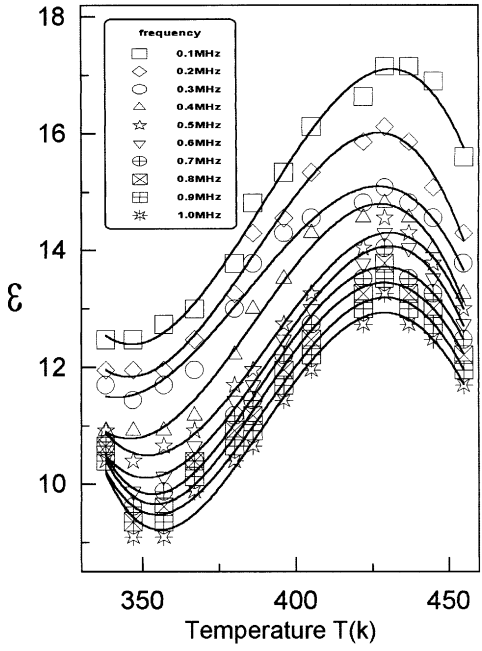

FIGURE 2 The dependence of the real part of the dielectric constant of irradiated dyed PVA for 1 minute on temperature as a function of frequency.

the crystalline region of the dyed PVA [1]. The increase of the dielectric constant with temperature is mainly due to an increase of the polarization arising from the increase of molecular motion of polymer chain segments. This motion facilitates the orientation of dipoles in the direction of the external applied electric field. The real part of dielectric constant of the dyed PVA decreases with increasing frequency till it reaches to frequency 0.5 MHz it suffers an abrupt increase in (ε') value. Then (ε') gives a slight decrease to reach a frequency 0.8 MHz at which it decreases with a rapid rate than in the range 0.6 – 0.8 MHz till reaching a frequency of 1 MHz. A peculiar behavior is obtained at 1.0 MHz where (ε') still greater than that at 0.2 MHz.

The dependence of the real part of dielectric constant (ε') of the dyed PVA on the temperature at different frequencies for samples irradiated with laser for 1 minute is illustrated in Figure 2. The S-shaped behavior of (ε') showed a peak at 429 K. The effect of frequency appears in the form of decreasing of (ε') of the material with different rates. Irradiating the samples with an increasing dose of laser increases the dielectric constant of the material where the first and second transition temperatures are not more pronounced. The third peak referring to the crystalline temperature was shifted with irradiation as in Figure 3. The relation indicates that a

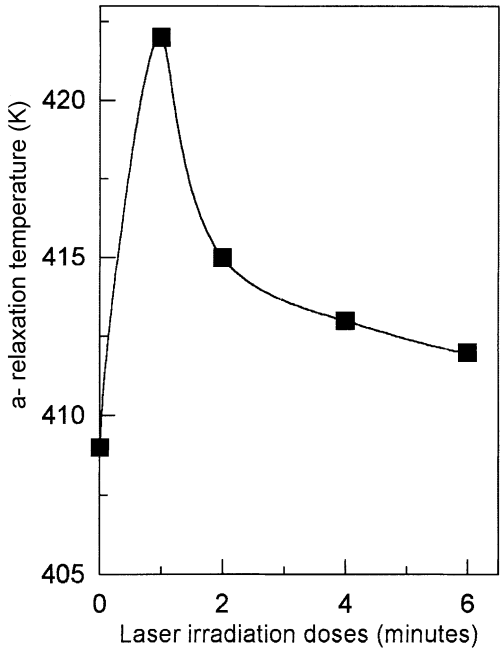

FIGURE 3 The α-relaxation temperature change with the laser irradiation time.

maximum crystalline temperature is obtained for samples irradiated for one minute and then decreases up to reaching to 6 minutes.

Much more interest was invested in measuring the dielectric properties of the materials in the frequency region where dispersion takes place. The dielectric constant falls off with rising frequency because the dipolar polarization can no longer change fast enough to reach equilibrium with the polarizing field. The frequency response of the dielectric constant of the material changes with frequency for different temperatures is shown in Figure 4. Same behavior as that of Figure 2 is obtained. At a certain temperature the increase of frequency decreases the dielectric constant till reaches a minimum value at 0.5 MHz which varies depending on the heating temperature. Further increase of frequency results in a sudden increase of the real part of the dielectric constant value at 0.6 MHz.

Figure 5 correlates the real part of the dielectric constant and frequency at different heating temperatures when irradiating the dyed PVA with the laser beam for 1 minute. The S-shape of the behavior disappeared. The increase of the frequency is meeting with a step decrease in the dielectric constant showing two transitions depending on the heating temperature.

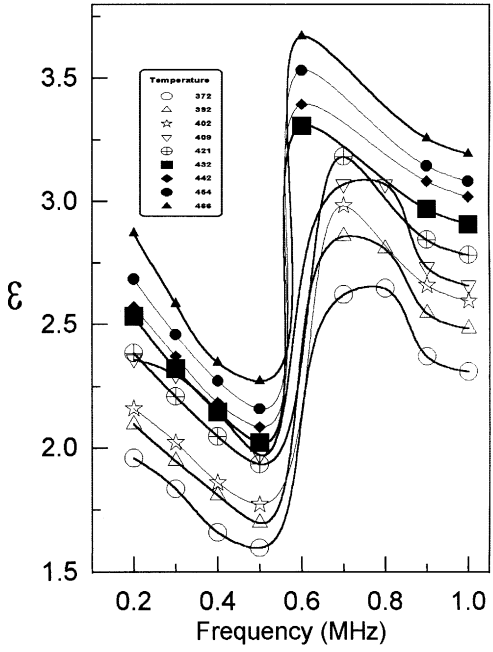

FIGURE 4 The dependence of the real part of the dielectric constant of unirradiated dyed PVA on frequency as function of temperature.

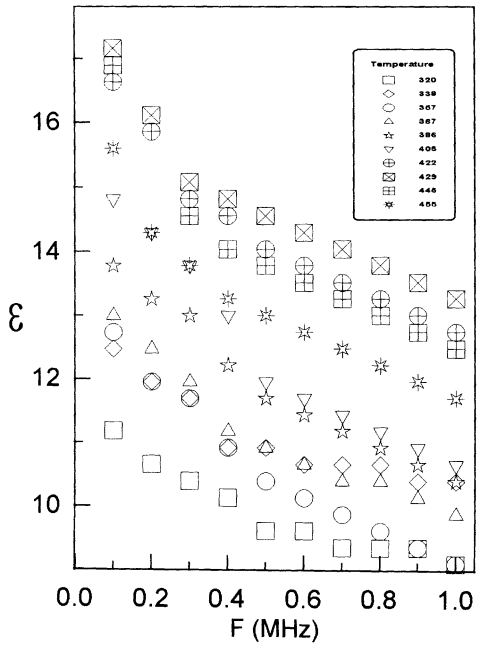

FIGURE 5 The dependence of the real part of the dielectric constant of irradiated dyed PVA with laser for 1 minute on 0 frequency as a function of temperature.

Increasing the temperature increases the dielectric constant values until reaches a temperature 385 K it decreases and then again continues to increase and at 429 K it decreases. The frequency anomalies appear as a change in the line slopes at these. Irradiating the dyed PVA for 2 minutes repeats the behavior of Figure 4 but the maximum temperature shifts to lower one. The S-shape behavior starts to appear upon irradiation for 4 and 6 minutes. This means that laser irradiation was made some change of the material where the dipole motion followed the field frequency. This appeared as an abrupt increase of the dielectric constant at a certain frequency and temperature.

The Cole–Cole diagram ($\varepsilon'' - \varepsilon'$) for the dyed PVA sample at temperature 310 K is shown as in Figure 6. The semicircle intercepts the real part of the dielectric constant (ε') axis in two points ε_∞ and ε_0 referring to optical and static values respectively [2]. Dyed PVA irradiated for different times 1, 2, 4 and 6 minutes has a similar Cole–Cole diagram with different values of ε_0 and ε_∞. The temperature dependence of the static and high frequency dielectric constants of the unirradiated dyed PVA is plotted as in Figure 7. The dc and high frequency dielectric constants reveal the presence of the glass transition temperature at 360 K and the second temperature at

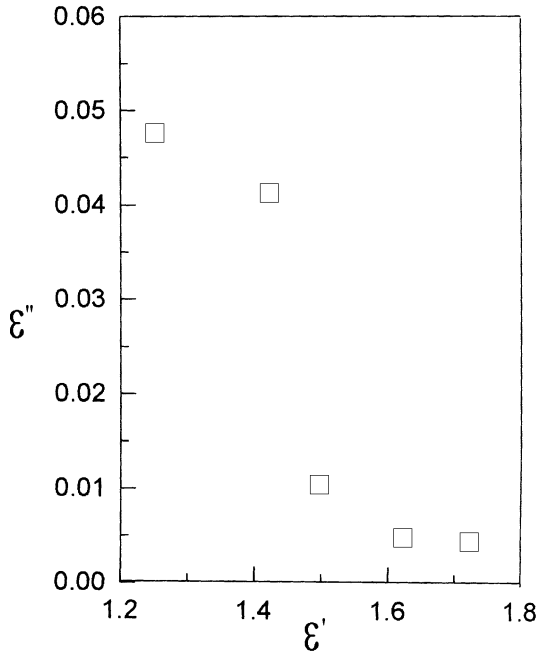

FIGURE 6 The Cole–Cole diagram for the unirradiated dyed PVA at temperature 310 K.

380 K. In addition a transition temperature at 409 K in the case of high frequency dielectric constant is obtained. The dc dielectric constant value of the irradiated dyed PVA for one minute is five orders greater than that of the unirradiated sample and the value slightly decreases with irradiation till reaches to 6 minutes irradiation it increases. The difference $(\varepsilon_0 - \varepsilon_\infty)$ at 360 K and 380 K is doubled when the sample irradiated for 1 minute. This difference gives an indication for the relaxation time through the unirradiated and irradiated dyed PVA. In addition to the relaxation time the Cole–Cole diagram gives the prediction about the value of the refractive index of the samples. The behavior of the refractive index under the effect of heating and irradiation with laser follows that of the high frequency dielectric constant.

A plot of the logarithm of ac electrical conductivity *versus* the reciprocal of the absolute temperature multiplied by the Boltzmann constant is shown in Figure 8 for unirradiated dyed PVA. This plot obeys the equation $\sigma = \sigma_0 \exp(-E/\mathrm{k}T)$, (where σ_0 is a constant, E is the activation energy and k is the Boltzmann constant). The ac conductivity gives the same anomalies as these obtained in the ε' data. The conductivity increases linearly with

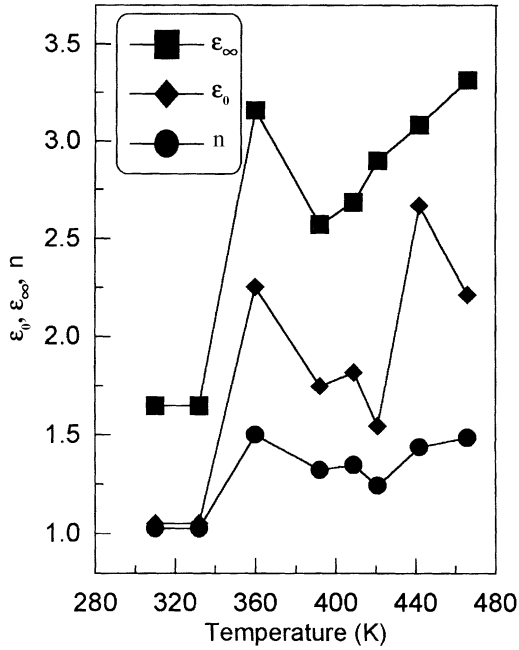

FIGURE 7 The correlation of static and high frequency dielectric constants and the refractive index of the unirradiated dyed PVA on temperature.

temperature (first or lower region of temperatures) and then suffers from a jump of its value (second or medium region of temperatures) and then continues its increase with temperature (third or higher region of temperatures). The relation has two breaks one at the beginning of the jump, which denotes the glass transition temperature. The second break is at the end of the jump which is related to the crystalline region [1]. The temperatures at the two breaks are changed with the external applied electric field frequency and also the slopes of the three lines.

The increase of the irradiation time causes a shift of the conductivity to higher value, as in Figure 9, up to 4 minutes where it decreases. The jump of the conductivity in the second region of temperature of unirradiated dyed PVA appears as a change in the slope only in the irradiated ones. For 6 minutes laser irradiation, the second region disappeared and one straight line was obtained. The slopes of the linear parts change. Values of the activation energies for the three regions were calculated and recorded in Table 1. From the table, it is clear that the activation energy indicates a resonance behavior at different frequencies. The resonance frequency shifts to lower ones with increasing irradiation times. Also the activation energy

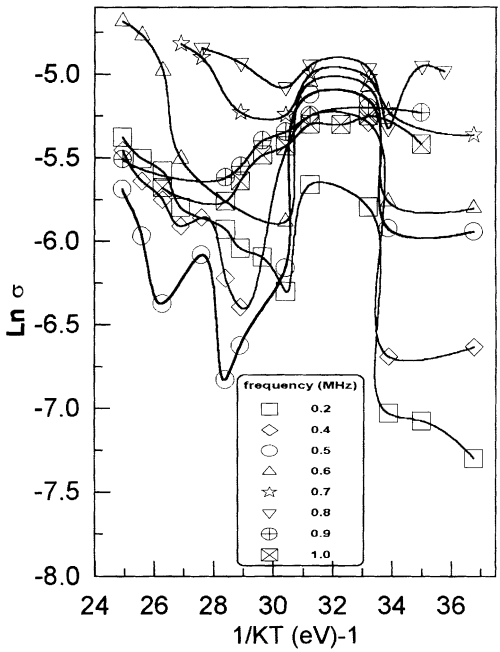

FIGURE 8 The a.c. conductivity change of the unirradiated dyed PVA with the reciprocal of the absolute temperature multiplied by Boltzmann constant.

values at the peaks increases with irradiation time till it reaches 2 minutes of irradiation at which it decreases again. Figure 10a represents the change of the activation energy in the second region with frequency. The unirradiated sample showed a gradually decrease in the activation energy with increasing the field frequency up to 0.5 MHz after which it increases. Irradiating the samples for different times, the behavior of the thermal activation energy against the frequency inflected showing a resonance's curves at frequency 0.5 MHz. Increasing the irradiation time up to 2 minutes increases the thermal activation energy and then it starts to decrease as in Figure 10b. This region of temperature contains the first crystalline temperature at about 386 K where its change with frequency was not pronounced in the real part of the dielectric constant.

Figure 11a illustrates the activation energy of the third region against the external applied frequency at different laser irradiation times. For all irradiation times the activation energy is sharply increases with frequency up to 0.4 MHz after which it decreases. The effect of the irradiation time on the activation energy for this temperature region can be traced by plotting the activation energy *versus* the irradiation time at the characteristic frequency

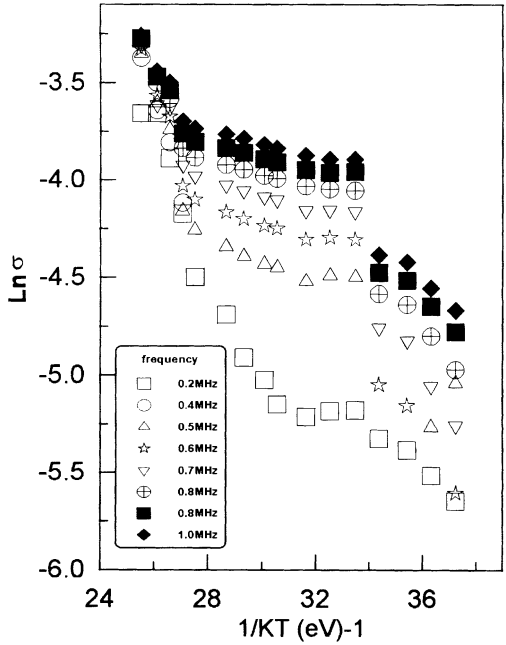

FIGURE 9 The a.c. conductivity change of the irradiated dyed PVA with laser for 1 minute against reciprocal of the absolute temperature multiplied by Boltzmann constant.

TABLE 1 The change of the activation energy of the first region with laser irradiation time for different frequencies

Frequency / *Irrad. time*	0 *minute*	1 *minutes*	2 *minutes*	4 *minutes*
0.2 MHz	0.097	0.118	0.043	0.274
0.3 MHz		0.075	0.028	0.298
0.4 MHz	0.020	0.090	0.030	0.599
0.5 MHz	0.006	0.175	0.613	0.158
0.6 MHz	0.014	0.311	0.629	0.116
0.7 MHz	0.050	0.301	0.439	0.142
0.8 MHz	0.044	0.216	0.224	0.077
0.9 MHz	0.016	0.190	0.038	0.096
1.0 MHz	0.093	0.181	0.035	0.085

0.4 MHz as in Figure 11b. The figure shows an increasing value of activation energy with irradiation time till reaches 1 minute after which it decreases. The increase in the activation energy may be due to the initiation of some defects by irradiation. These defects are expected to appear in a form of

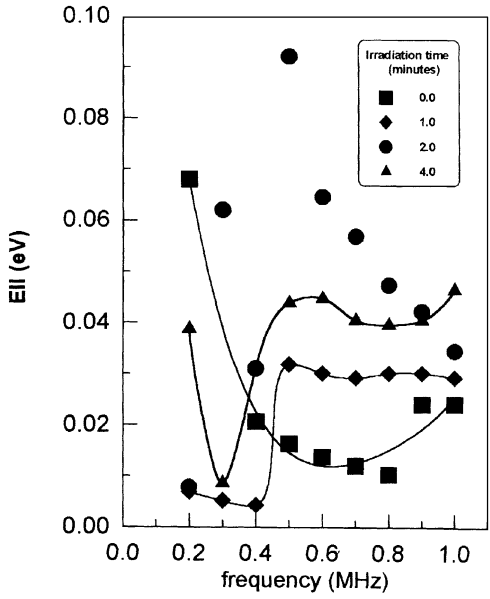

FIGURE 10a The change of the activation energy of the second region E_{II} with frequency 0.5 MHz on the laser irradiation times.

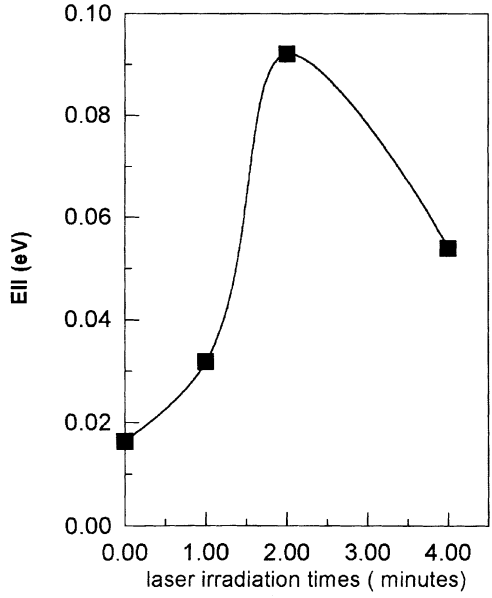

FIGURE 10b The dependence of the activation energy E_{II} of second region with frequency 0.5 MHz on the laser irradiation times.

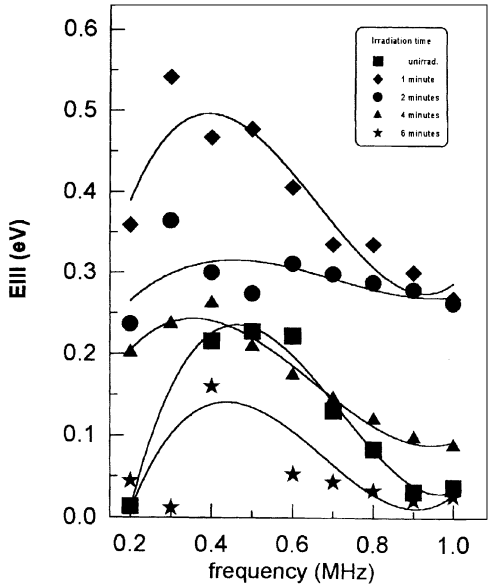

FIGURE 11a The change of the activation energy of the third region E_{III} with frequency for different laser irradiation times.

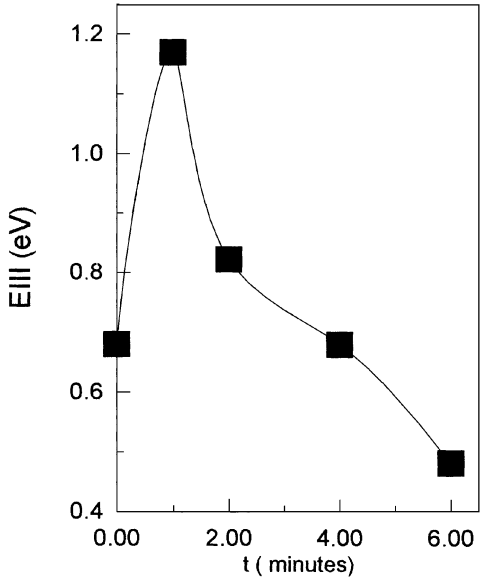

FIGURE 11b The change of the activation energy of the third region E_{III} at resonance of 0.4 MHz for different laser irradiation times.

degradation. After 1-minute irradiation, the recovering effect takes place in which the conductivity increases.

CONCLUSION

Finally, one may conclude that, the ac conductivity is very sensitive to the transition that takes place in the samples. The laser irradiation of sample for 1 minute increases the activation energy causing the chain scission of the polymer. This gives a chance for the chains to reorient in the field direction enhancing the decrease of the sample crystallinity. Consequently this increases the temperature at which the crystallinity starts to decrease at 429 K as in Figure 11b. This reorientation increases the real part of the dielectric constant ε^b as in Figure 2. Moreover optimization condition becomes complete when applying a frequency of 0.4 MHz. The crosslinking of samples predominates during further increase of irradiation time up to 6 minutes. Irradiation with laser for 2 minutes gives maximum activation energy for the second region of temperature at a frequency of 0.5 MHz causing the sample degradation. Crosslinking of the sample takes place after irradiation for over 2 minutes.

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