Optical Absorption and Thermally Stimulated Depolarization Current Studies of Nickel Chloride-Doped Poly(vinyl alcohol) Irradiated with Low-Level Fast Neutron Doses

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SYNOPSIS

The influence of neutron irradiation on ultraviolet/visible absorption and thermally stimulated depolarization current in nickel chloride–poly(vinyl alcohol) (PVA) cast films has been investigated. The spectral measurements indicate the responsibility of the Ni^{2+} ion in its octahedral symmetry. Dopant concentrations higher than 10 wt % $\mathrm{Ni\ Cl_2}$ are found to make the samples more resistant to a degradation effect caused by neutron irradiation. The thermally stimulated depolarization currents (TSDC) of pure PVA revealed the existence of the glass transition T_g and space charge relaxation peaks, whereas doped-PVA samples show a new sub-T_g relaxation peak. A proposed mechanism is introduced to account for the neutron effects on both glass transition and space charge relaxation peaks. The peak positions, peak currents, and stored charges of the sub-T_g relaxation peak are strongly affected by both the concentration of the dopant and neutron exposure doses.

INTRODUCTION

Metal-insulator systems have been the subject of both theoretical and experimental interests because of their increasing technological importance. Depending on the chemical nature of the doping substances and the way in which they interact with the host matrix, the dopant alters the physical properties to different degrees.[1-5] Exposure of polymers to fast neutron radiation causes changes in structure and, hence, in chemical and physical properties.[6-9]

The structural response of thermally stimulated depolarization currents (TSDC) in polymers due to γ-radiation has been confirmed with satisfactory results.[10,11] To our knowledge, no attempt has been made to study the effect of neutron fluence on the depolarization behavior of doped polymers. On the other hand, little work[12,13] has been done on the effect of neutron and γ-radiations on the optical properties of metal halide-doped polymers. Hence, in the present work, it was proposed to study the effect of low-level neutron fluences on the characteristic TSDC thermogram and optical absorption of poly(vinyl alcohol) films doped with different amounts of nickel chloride.

EXPERIMENTAL

Poly(vinyl alcohol) (PVA) films doped with different percents including 5, 10, 20, and 40% by weight of $NiCl_2 \cdot 6H_2O$ were made using a cast method given elsewhere.[2,13] Samples were irradiated at room temperature with fast neutrons from a ^{252}Cf source over the range 10^5–10^8 n/cm^2. The neutron fluence at the position of exposure was measured by the use of calibrated ^{115}LR-track detectors. Ultraviolet-visible spectra were obtained using a Perkin-Elmer 4B spectrophotometer over the range 200–900 nm. Thermally stimulated depolarization current studies

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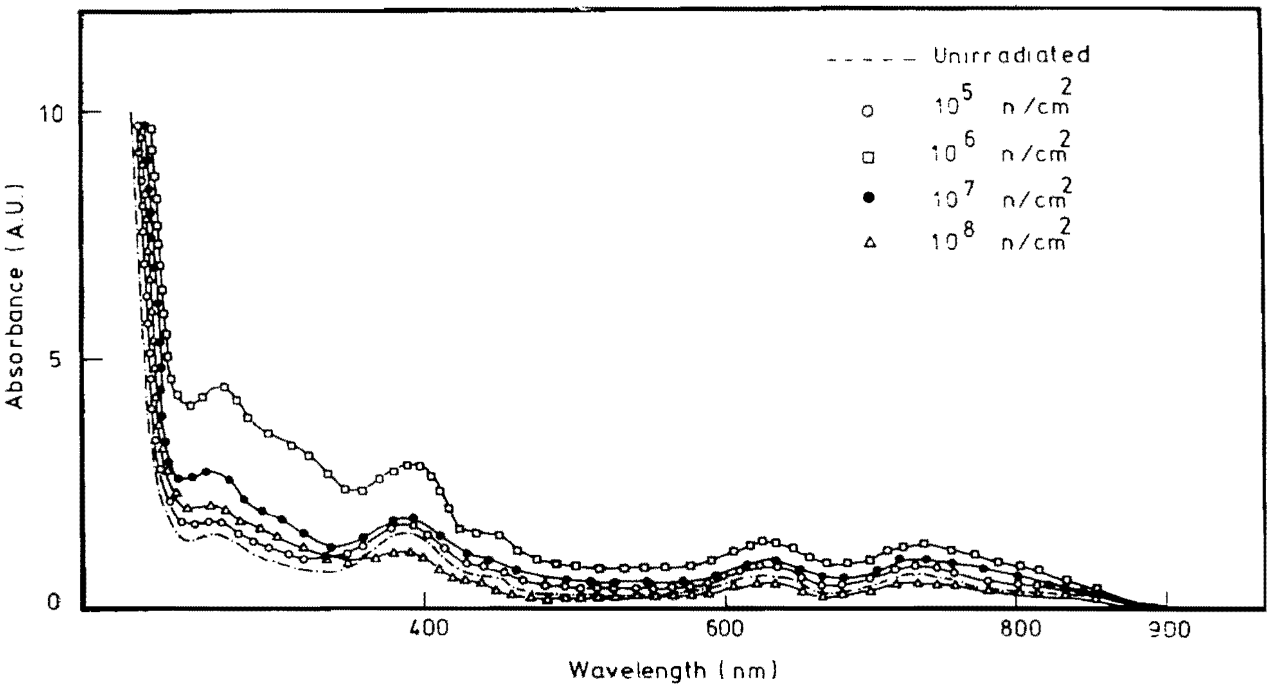

Figure 1 Absorption spectra of PVA doped with 20 wt % $NiCl_2$ irradiated with different neutron fluences. Film thickness 0.2 mm.

were done in the sandwich configuration with an effective area of 1.80 cm^2. Before TSDC measurements, polarization of samples was carried out by first heating them to a specific polarizing temperature T_p = 373 K and then applying an electric polarizing field E_p = 2 kV/cm for a polarizing time t_p = 2 h. After polarization, the samples were cooled to room temperature with the field on. Then, the field was switched off at room temperature and the samples were shorted for about 1 day to remove frictional and stray charges,[14] if any. A Keithley Electrometer Model 616 was used to measure the subsequent depolarization current at different temperatures of the sample. The heating rate was 1.5°C/min.

RESULTS AND DISCUSSION

Optical Absorption

Optical absorption measurements are carried out in particular to check the presence of the nickel ionic form in the polymer matrix. The ultraviolet/visible absorption spectra of 20 wt % $NiCl_2$-doped PVA films before and after exposure to various neutron fluences in the range 10^5–10^8 n/cm^2 are shown in Figure 1. In all, five bands have been observed in the visible and near the ultraviolet regions around 722, 646, 464, 400, and 275 nm. The assigned band positions for the other doped concentrations of 5, 10, and 40 wt % $NiCl_2$ were found to be similar and therefore are not presented here. It is well known[15] that Ni in the octahedral symmetrical field possesses three spin-allowed transitions and two spin-forbidden transitions as well. Accordingly, it is reasonable to assign the absorption bands observed at 722 and 400 nm to the spin-allowed transitions ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$, ν_2, and ${}^3T_{1g}(p) \leftarrow {}^3A_{2g}$, ν_3, respectively. The third spin-allowed transition is not observed in our spectra because it appears at a wavelength (1200 nm) that is out of range of the spectrophotometer used. On the other hand, the assignment of the bands at 646 and 464 nm definitely corresponds to the spin-forbidden transitions ${}^1E_g \leftarrow {}^3A_{2g}$ and ${}^1T_{2g} \leftarrow {}^3A_{2g}$, respectively. The ${}^1E_g$ and ${}^1T_{2g}$ states are accidentally degenerate. The appearance of spin-forbidden transitions is a direct consequence of the presence of spin-orbit coupling. The most intense band observed at 275 nm belongs to the ligand PVA matrix.[9] From the nature and the position of the bands, it can be assumed that the Ni^{2+} ion in its octahedral symmetry is responsible for the observed spectrum.

Using the transition energy ratio diagram[15] ν_3/ν_2 vs. Dq/B and $E(\nu_3)/B$, the values of the Racah interelectronic parameter B and the ligand field strength Dq are found to be 929 and 864 cm^{-1}, respectively. The predicted values ν_1 (10 Dq) lies at 8640 cm^{-1}, which is near to that found in the literature.[16] The decrease in the value of B in comparison with the corresponding free-ion value 1041 cm^{-1} indicates the increasing degree of overlapping between wave functions of Ni ions and that of the ligand OH groups.

No observable shift in the position of the bands is observed either by neutron irradiation or by increasing the nickel concentrations (figures not shown). However, the absorption intensity of the bands shows remarkable variation due to both neutron irradiation and the nickel concentrations. It can be seen from Figure 2 that the absorbance at wavelengths 275 and 400 nm for the doped samples up to 10 wt % $NiCl_2$ increases on irradiation by 10^5 n/cm^2 and then decreases with exposure doses up to 10^8 n/cm^2. However, at higher concentrations of 20 and 40 wt % $NiCl_2$, the absorbance at wavelengths 275 and 400 nm increases with increasing neutron fluence up to 10^6 n/cm^2, followed by a decrease up to 10^8 n/cm^2. Therefore, the increase of dopant concentrations above 10 wt % $NiCl_2$ appears to make the sample more resistant to degradation effects usually caused by neutron irradiation. This may allow one to conclude that there is a limiting concentration beyond which more energy is transferred to the polymer, yielding a rupture of the bonds in the polymer matrix. Hence, it is recommended to take into consideration the role of additive concentration of chemical compounds in obtaining polymeric materials with specific characterization.

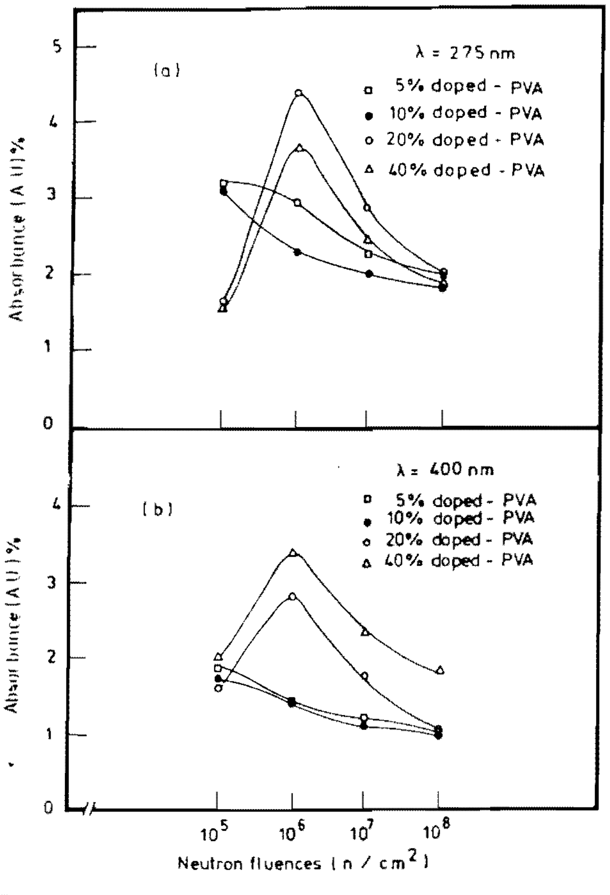

Figure 2 Variation of absorbance as a function of neutron fluences at (a) λ = 275 nm and (b) λ = 400 nm for $NiCl_2$-doped PVA specimens.

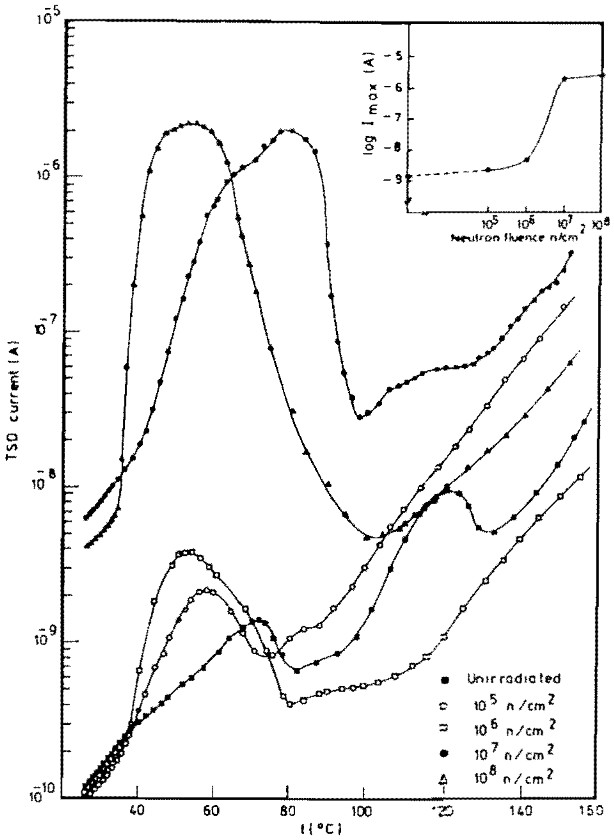

Figure 3 Temperature dependence of TSDC for pure PVA at different neutron fluences.

Thermally Stimulated Depolarization Currents

The TSDC method is now widely accepted as a very sensitive probe of all the temperature-dependent relaxations, allowing one to obtain a complete picture of the kinetic transitions, local mode motions, and space charge polarization[17,18] in one heating cycle.

The TSDC spectra of unirradiated and irradiated films of the PVA–$NiCl_2$ system were studied. Figure 3 shows the TSDC spectra for the pure PVA samples

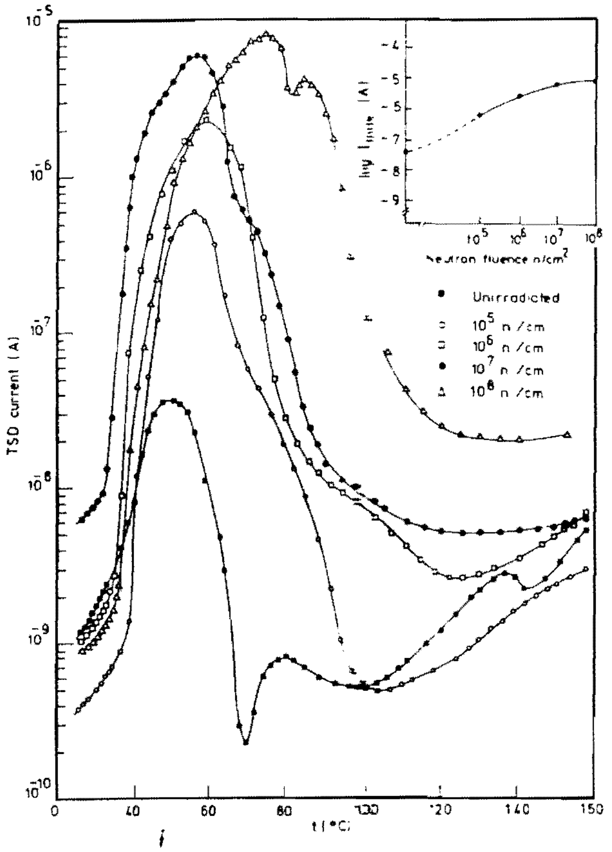

Figure 4 Temperature dependence of TSDC doped PVA with 5 wt % $NiCl_2$ at different neutron fluences.

before and after irradiation with fast neutron fluences in the range 10^5–10^8 n/cm². All samples are characterized by the occurrence of one distinct discharge current peak except the unirradiated one, which has two current peaks. This result found for the unirradiated sample is generally consistent with those previously reported in the literature.[19,20] The low-temperature peak at about 72°C is preferably attributed to the glass transition (T_g) relaxational process resulting from micro-Brownian motion of the main-chain backbone. The peak observed at a higher temperature of about 122°C is suggested to be associated with a space-charge polarization due to charge generation at the electrode–sample interface and also due to motion of the excess charge arising from the increased chain mobility.[21,22] Upon irradiation, the space-charge relaxation peak vanishes, while the T_g relaxation peak showed a large increase in the current peak. Further, the peak position of the latter one is found to be associated with a remarkable shift toward lower temperatures, except that at the neutron fluence of 10^7 n/cm², which exhibited a small shift toward higher temperature. In addition, the broadening of the peak is remarkably neutron fluence-dependent. This might be due to the creation and increase in the number of trapped ions and free radicals that predominate due to the destruction of the dipoles, with relatively higher doses. These effects depend mainly on the total quantity of energy deposited in the polymer, regardless of the nature of the incident radiation.[23]

For the 5 wt % doped unirradiated sample, a new peak has been developed at about 48°C, in addition to the ordinary peaks at about 80 and 136°C (see Fig. 4). Neutron irradiation is found to remove the ordinary two peaks, except at the fluence of 10^8 n/cm², which entails the appearance of the low-temperature T_g ordinary peak. It is observed that on increasing neutron fluences the current peak with differing profiles increased and shifted toward higher temperatures. The change in shape of the current peak may result from a variation in the distribution function of the associated relaxation times. Figure 5 shows that the samples doped with 10 wt % dopant have similar behavior except that the T_g relaxation peak reappeared at the neutron fluence of 10^6 n/cm². Further concentrations of 20 and 40 wt % $NiCl_2$ keep the general behavior of unirradiated samples

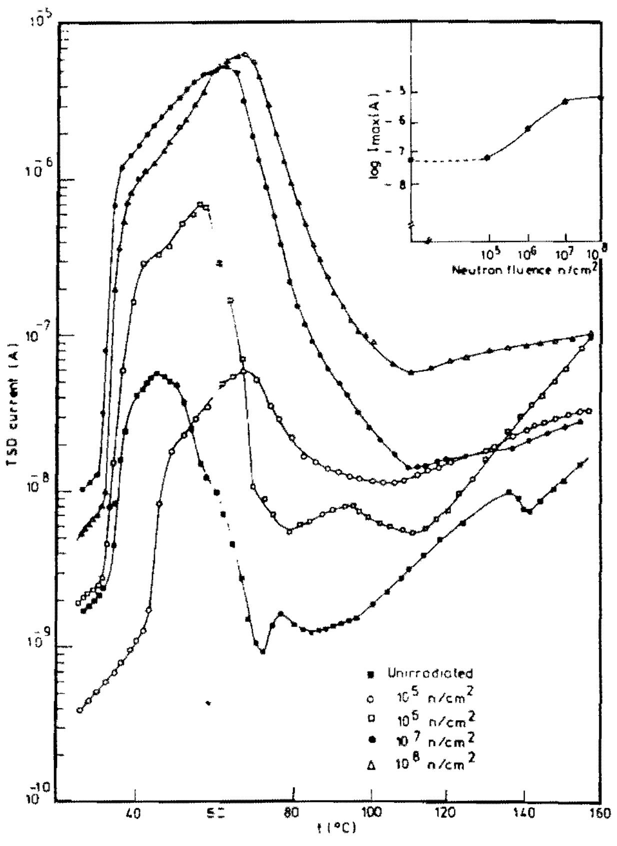

Figure 5 Temperature dependence of TSDC for PVA doped with 10 wt % $NiCl_2$ at different neutron fluences.

nearly unchanged. During this, the intensity of the T_g and space charge relaxation peaks appeared to be more pronounced (see Figs. 6 and 7). On irradiation, the T_g and space charge relaxation peaks disappeared except that the T_g relaxation peak is observed more remarkably at 10^7 n/cm^2 and at 10^6 n/cm^2 for 20 and 40 wt % dopant, respectively. The magnitude of the current peak increases irregularly with neutron fluences and the position is shifted toward the high-temperature side.

The addition of $NiCl_2$ to PVA affects greatly the shape of TSDC spectra and leads to a new relaxation peak situated between 40 and 60°C depending on the amount of dopant. This peak is not observed in the previous work of Basha et al.,[2,20] probably because of several factors including the difference in polarization conditions, the rate of heating, and the long time of shorting the sample. The strength of the new peak increased on increasing the concentration of the dopant in the polymer matrix for unirradiated samples (see Figs. 3–7). This new peak observed at the low-temperature end of the glass transition T_g relaxation peak is probably related to the so-called sub-T_g intermediate relaxation, which has been reported to appear in a number of polymers as a nonequilibrium shoulder on the dissipation curves over the temperature range of 40–80°C in low-frequency measurements.[24–26] It seems that this kind of relaxation should be considered as a proximate nonequilibrium precursor of glass transition,[27] but little is known until now about its detailed behavior and molecular mechanism. In our experiments, in particular, it remains unclear why it appears with adding the dopant to the PVA matrix.

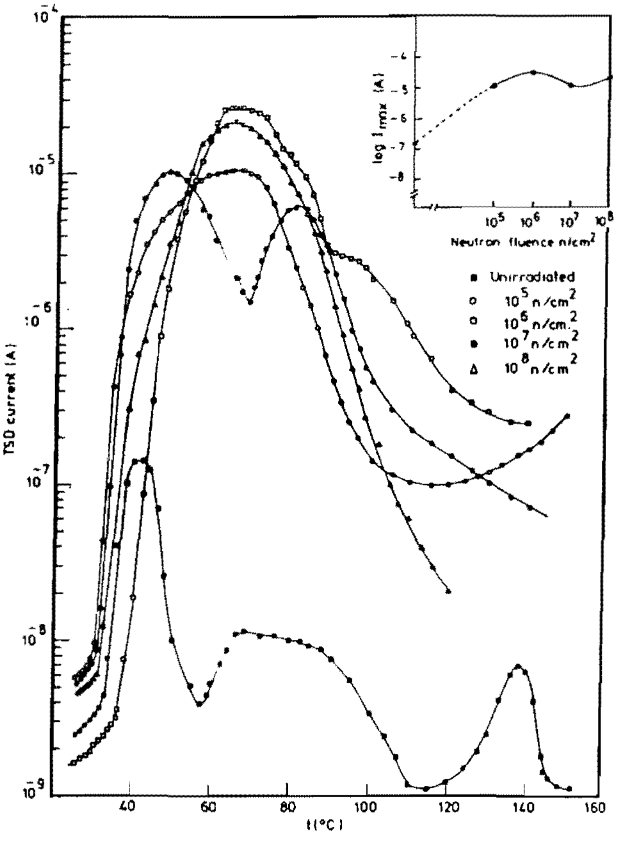

Figure 6 Temperature dependence of TSDC for doped PVA with 20 wt % $NiCl_2$ at different neutron fluences.

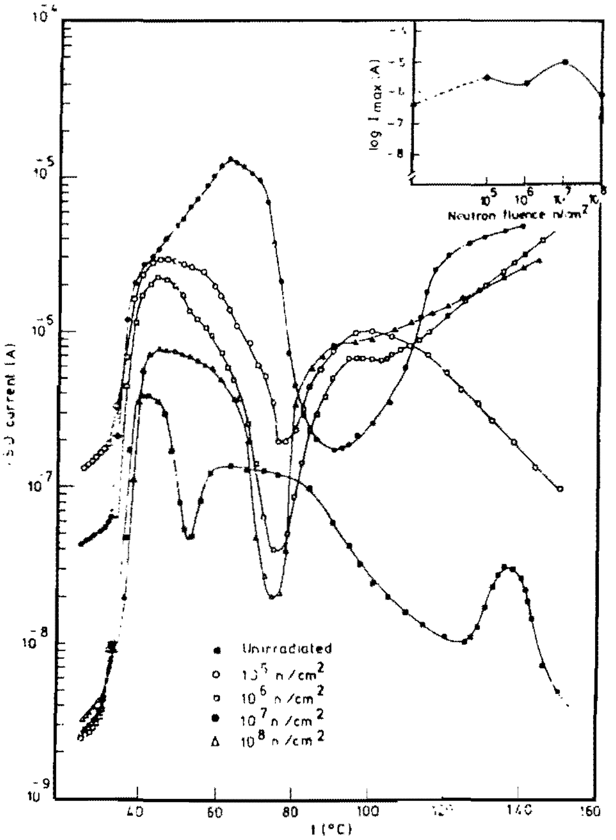

Figure 7 Temperature dependence of TSDC for doped PVA with 40 wt % $NiCL_2$ of different neutron fluences.

The disappearance of the high-temperature region peak on irradiation may be due to the slowly decaying space charge. It is worthwhile to remember that the disappearance of the T_g relaxation peak at most neutron fluences for each sample and the variation of the magnitude of the sub-T_g relaxation peak, together with a shift in its position to higher temperature, may all give an indication of structural modifications. It should be noted that both crosslinking and degradation processes induced by neutron irradiation occur simultaneously, one or the other generally being dominant.

Finally, from the results obtained in this work, it can be concluded that the structure of nickel chloride doped-poly(vinyl alcohol) samples irradiated with fast neutron fluences in the range 10^5–10^8 n/cm^2 is changed. This is clearly shown by the change of absorbance in the ultraviolet/visible spectra and is confirmed by the analysis of the TSDC spectra. These changes evidently are due to the action of fission neutrons on the sample that results in ion recoils and free radicals through elastic collision with the structural arrangement of the molecules. The ions and free radicals are not stable but cause further reactions that may result in either breakdown of the polymer molecules (degradation) or in the formation of new molecules by combination between themselves or with molecules of other substances (polymerization and cross-linking).

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