



## Effect of gamma irradiation on the etching and optical properties of a newly developed nuclear track detector called (PNADAC) homopolymer

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### ABSTRACT

In the present work, we have determined the bulk-etch rates of a newly developed track detector called poly-[*N*-allyloxycarbonyl diethanolamine-bis allylcarbonate] (PNADAC) homopolymer at different temperatures to deduce its activation energy. The energy of activation is found to be  $(1.02 \pm 0.04)$  eV. This compares very well with the values of activation energy reported in the literature for the most commonly used nuclear track detectors. The effects of gamma irradiation on this new detector in the dose range of 4.7–14.5 Mrad have also been studied using UV–visible spectroscopic technique. The optical band gaps of the unirradiated and the gamma-irradiated detectors determined from the UV–visible spectra were found to decrease with the increase in gamma dose. These results have been explained on the basis of scission of the detector due to gamma irradiation.

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### 1. Introduction

To indigenously prepare plastic materials for solid-state nuclear track detection applications, a new polymer that is a homopolymer of *N*-allyloxycarbonyl diethanolamine-bis allylcarbonate (NADAC) monomer was prepared recently by us (Mascarenhas et al., 2006). A preliminary study on the etching conditions and track detection characteristics of this detector was also carried out. The knowledge of bulk-etch rates for the nuclear track detectors at different temperatures is of considerable usefulness (Dwivedi and Mukherji, 1979). It can also be used for the evaluation of activation energy for bulk etching and this is very often determined for nuclear track detectors (Dwivedi and Mukherji, 1979; Neerja Prasher and Singh, 2007; Agarwal et al., 2006; Nikezic and Yu, 2004). In the present work, we have therefore determined the bulk-etch rates of this newly developed track detector at different temperatures to deduce the activation energy for bulk etching. The demand for polymers having improved surface and bulk properties is continuously on the rise due to their use for various scientific and technological applications (Henshaw, 1982; Tuross et al., 2003). Irradiation of polymers has established itself as one of the most acceptable approach to alter polymer properties significantly (Laskarakis et al., 2004; Taupiac et al., 1997; Mujahid et al., 2005; Calcagno et al., 1992;

Steckenreiter et al., 1997). When an ionizing radiation passes through a polymer, the incident energy is transferred to the medium as a result of primary ionization and excitation of the target molecules. These ionization and excitation processes inside the target leads to breaking of original bonds, production of excited and ionized species, chain scission, radical formation, bond rearrangement, etc. (Lee, 1999; Mokrani et al., 2003). All these processes are responsible for the modification of chemical, electrical, optical and mechanical properties of polymers leading to their applications in different scientific and technological fields. The effects of gamma irradiation on this new detector in the dose range of 4.7–14.5 Mrad have therefore been studied by using UV–visible spectroscopic technique. The optical band gaps of the unirradiated and the gamma-irradiated detectors were determined from the UV–visible spectra.

### 2. Experimental

Generally, the changes in thickness and weight methods are used for the determination of bulk etch rate,  $V_b$ . The change in thickness method involves the measurement of thickness at regular intervals of etching, whereas the change in weight method involves decrease in weight of the film upon etching. In order to use the thickness method, the film should be of uniform thickness throughout. The films of the poly-[*N*-allyloxycarbonyl diethanolamine-bis allylcarbonate] (PNADAC) homopolymer were studied for their initial thickness. It was observed that the homopolymer

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films had somewhat higher variation (about 10%) in the film thickness. Taking into account the fact that the change in thickness of the films upon etching was less than the standard deviation observed in the initial thickness of the films, it was decided to use the change in weight method instead of the change in thickness method for the evaluation of the bulk etch rate (Sharma et al., 1991). Eq. (1) given below was used for the  $V_b$  measurements.

$$V_b = (M_1 - M_2)T_i/2M_1t \quad (1)$$

where  $M_1$  and  $M_2$  are the initial and final weights of the films,  $t$  is the etching time and  $T_i$  is the initial thickness. The bulk etch rates were determined at different temperatures by the chemical etching technique to deduce activation energy for bulk etching. In this technique, a sample of known weight and thickness was dipped into the etchant (6N NaOH), maintained at a fixed temperature in a thermostat, under condition of stirring, for accurately noted time period. It was then taken out, thoroughly washed with demineralized water and after air drying at room temperature was weighed again. These operations were repeated at each temperature and  $V_b$  was calculated by making use of Eq. (1). The effects of gamma irradiation on the (PNADAC) homopolymer detector (thickness 615  $\mu\text{m}$ ) in the dose range of 4.7–14.5 Mrad were studied by UV–visible spectroscopy. For the gamma irradiation, the detector pieces each of size about 2  $\text{cm}^2$  in area were cut and these samples were irradiated with Co-60 gamma rays in the gamma irradiator of Radiochemistry Division, BARC for doses of 4.7, 8.1 and 14.5 Mrad. UV–visible spectra by a UV–VIS Spectrometer (Jasco, Model V-530) in the range of 200–800 nm of unirradiated and gamma irradiated samples in the above dose range were recorded to study the changes induced in the detectors by gamma irradiation. The detector samples used in the present studies were not degassed. However, the samples had been covered with a thin film of polyester before using them to protect it from atmospheric gases particularly from radon and thoron. These gases increase the alpha background of the detector.

### 3. Results and discussion

The values of bulk etch rate determined by the above given method at the temperatures 70, 75 and 80 °C for the new detector (PNADAC) homopolymer were found to be  $0.60 \pm 0.06$ ,  $0.90 \pm 0.05$  and  $1.50 \pm 0.10 \mu\text{m}/\text{h}$ , respectively. For calculating the activation energy for bulk etching, the bulk etch rates were determined at different temperatures. In Fig. 1, we have plotted  $\log V_b$  against the reciprocals of the absolute temperatures for the unirradiated (PNADAC) homopolymer. These plots conform to the expression  $V_b = Ae^{-E/kT}$ , where  $E$  is the activation energy for bulk etching,  $A$  is a constant for a given medium–etchant combination,  $k$  is the Boltzmann constant and  $T$  the temperature in K. The activation energy,  $E$  value, obtained for the (PNADAC) homopolymer is  $(1.02 \pm 0.04)\text{eV}$  and it is given in Table 1 along with the  $E$  values reported in the literature for some commonly used nuclear track detectors (Dwivedi and Mukherji, 1979; Neerja Prasher and Singh, 2007; Agarwal et al., 2006; Nikezic and Yu, 2004). There seems to be good agreement between the values obtained by us for the new track detector and the values reported for the most commonly used track detectors. A slightly higher activation energy observed in the present work may possibly be due to a small difference in the concentration of the etchant used (Dwivedi and Mukherji, 1979). The UV–visible absorption spectra of the unirradiated and the gamma irradiated samples in the wavelength range 250–600 nm are presented in Fig. 2. Fig. 3 shows the variation

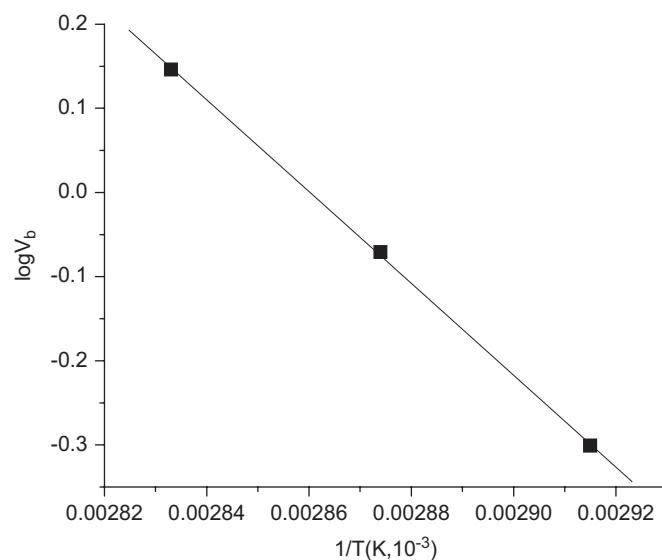


Fig. 1. The plot of  $\log V_b$  vs.  $1/T$  for unirradiated PNADAC homopolymer.

Table 1

Value of the activation energy for bulk etching of the new track detector (PNADAC) homopolymer along with the values reported in the literature for the commonly used nuclear track detectors

Nuclear track detector	Activation energy for bulk etching, $E$ (eV)
PNADAC homopolymer	$1.02 \pm 0.04$ (present work)
Lexan	$0.75 \pm 0.04$ (Dwivedi and Mukherji, 1979)
Cellulose acetate	$0.95 \pm 0.01$ (Dwivedi and Mukherji, 1979)
Lexan	$0.74 \pm$ not quoted (Neerja Prasher and Singh, 2007)
Polyester	$0.94 \pm$ not quoted (Agarwal et al., 2006)
Makrofol KG	$0.99 \pm 0.04$ (Nikezic and Yu, 2004)
Makrofol KL	$1.18 \pm 0.08$ (Nikezic and Yu, 2004)
Makrofol N	$0.89 \pm 0.04$ (Nikezic and Yu, 2004)
CR-39 (Pittsburgh)	$0.85 \pm 0.05$ (Nikezic and Yu, 2004)
CR-39 (Type unknown)	$0.92 \pm$ not quoted (Nikezic and Yu, 2004)
CR-39 (Homalite)	$0.89 \pm 0.04$ (Nikezic and Yu, 2004)
CR-39 (Homalite)	$0.83 \pm 0.04$ (Nikezic and Yu, 2004)
CR-39 (Pershore)	$0.78 \pm 0.03$ (Nikezic and Yu, 2004)
CR-39 (Pershore)	$0.79 \pm 0.02$ (Nikezic and Yu, 2004)
CR-39 (Pershore)	$0.77 \pm 0.02$ (Nikezic and Yu, 2004)
CR-39 (Pershore)	$0.79 \pm 0.02$ (Nikezic and Yu, 2004)
CR-39 (Pershore)	$0.80 \pm 0.01$ (Nikezic and Yu, 2004)

of absorbance difference with gamma dose at a characteristic wavelength of 342 nm. Absorbance difference for the gamma-irradiated samples with respect to unirradiated sample is maximum at 342 nm. So we have chosen this wavelength as the characteristics wavelength. The maximum relative standard deviation (RSD) on the optical response is about 5%. It is clear from Fig. 2 that the absorption edge is moving toward the longer wavelength at a higher dose of gamma rays. The optical band gaps ( $E_g$ ) of the unirradiated sample, 4.7, 8.1 and 14.5 Mrad gamma irradiated samples calculated from the change in optical wavelength (Singh and Prasher, 2005), are found to be  $4.28 \pm 0.03$ ,  $3.96 \pm 0.02$ ,  $3.75 \pm 0.03$  and  $3.63 \pm 0.02$  eV, respectively. For UV–visible studies, triplicate measurements were done on each sample. Hence each  $E_g$  value is a mean of three determinations. The maximum RSD obtained on  $E_g$  values is about 1%. It is clear that optical band gap decreases with increase in gamma dose. The decrease in  $E_g$  may be due to the production of free radicals and ions as a result of chain scission. Similar studies have been carried out earlier by other workers on the effect of irradiation on

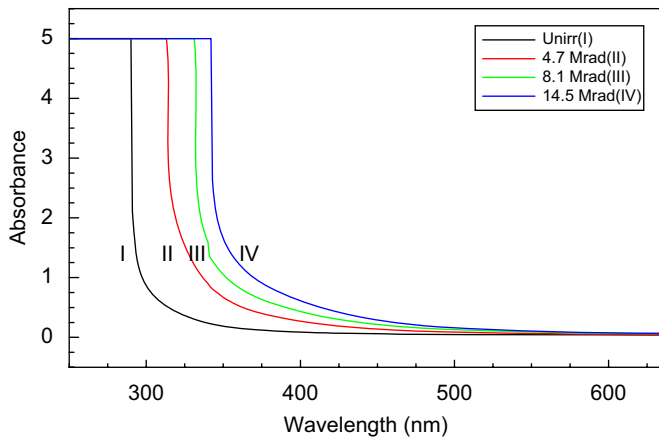


Fig. 2. Absorbance vs. wavelength for different gamma doses.

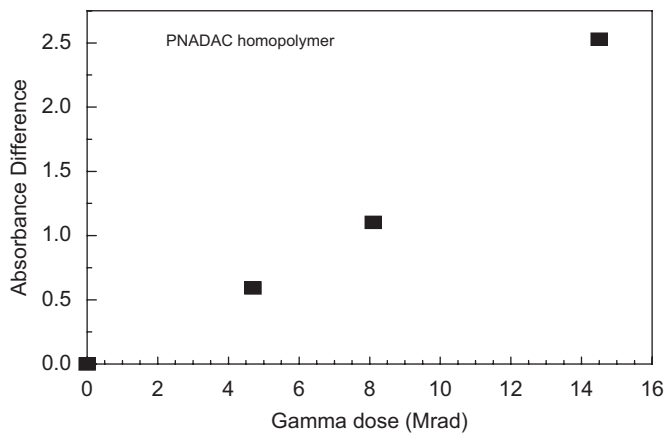


Fig. 3. Characteristics absorbance difference vs. gamma doses at 342 nm.

properties of polymers (Singh et al., 2003; Phukan et al., 2003; Marletta, 1990; Davenas et al., 1988; Lee et al., 1993; Alegaonkar et al., 2002; Sharma et al., 2007; Singh and Prasher, 2004a,b, 2005). In these studies, the polymer irradiation leads to shift in optical absorption edges, which indicates a lowering of the optical band gap (Phukan et al., 2003; Sharma et al., 2007; Singh and Prasher, 2004a,b, 2005). The decrease in optical band gap can imply an increase in conductivity of the irradiated polymers.

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