

Designing novel polymers for solid-state nuclear track detection (SSNTD), I: novel homo- and co-polymers with allyl diglycol carbonate from N-allyloxycarbonyl diethanolamine-bis(allylcarbonate)

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Abstract—A novel monomer, N-allyloxycarbonyl diethanolamine-bis(allylcarbonate), has been synthesized and cast-polymerized for the first time to obtain poly-[N-allyloxycarbonyl diethanolamine-bis(allylcarbonate)] (PNADAC), which was used successfully as a solid-state nuclear track detector for alpha particles and fission fragments. The monomer has been synthesized from diethanolamine by reacting allyl chloroformate in a one-step process. The kinetics of its polymerization reactions were studied. A co-polymer with allyl diglycol carbonate (ADC) was also prepared after studying the kinetics of the polymerization reaction. It was found that the homo- and co-polymers are more sensitive towards alpha particles as compared to the commercially available CR-39TM track detector.

Keywords: Solid-state nuclear track detection (SSNTD); N-allyloxycarbonyl diethanolamine-bis(allylcarbonate), poly-[N-allyloxycarbonyl diethanolamine-bis(allylcarbonate)]; diethanolamine; detectors; polymerization; nuclear tracks, dosimetry.

1. INTRODUCTION

The field of solid state nuclear track detection (SSNTD) is nearly half a century old. This technique for permanently recording the tracks of ionizing particles in insulating solids was discovered by Young [1] in 1958. Many insulating materials were subsequently tested, *viz.*, various minerals, glasses and polymers.

The most useful among these were found to be the plastic materials due to the ease with which the nuclear tracks could be revealed by the simple method of chemical etching and by viewing them under an optical microscope. The plastic materials

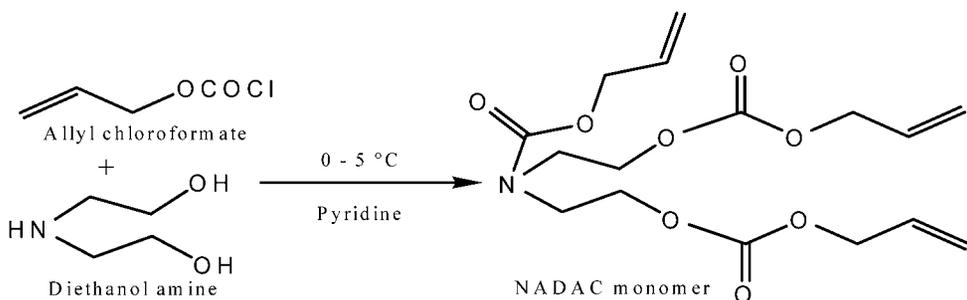
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most commonly used as nuclear track detectors at present are cellulose nitrate [2] (LR-115)TM, poly(allyl diglycol carbonate) (PADC) (CR-39)TM [3] and bisphenol A polycarbonates (Lexan)TM. Efforts were carried out to generalize the observations in terms of the sensitivity of a particular material to a charged particle and its structural features [4–6]. It was found that (1) all polymers containing aromatic rings tend to show lower sensitivity, (2) the highly cross-linked thermosets and the amorphous polymers show better sensitivity, (3) chain bridging the carbonate moieties can be crucial for sensitivity, (4) materials having one of the functional groups like $-\text{ONO}_2$, $-\text{CO}_3-$, $-\text{SO}_2-$ and $-\text{SO}_3-$ have been found to be more sensitive, (5) the density of the cross-links in the polymer matrix was also an important factor and (6) for PADC (CR-39)TM, it is known that the co-polymers are more sensitive than homo-polymers. The literature, however, shows that most of the efforts have been directed towards testing the available plastic materials for various SSNTD applications, rather than systematic designing of the newer monomers and polymers for SSNTD applications [7, 8]. It was, therefore, thought that polymers prepared from a hexafunctional monomer or a mixture of monomers would result in a material with high density of cross-links and probably even more amorphous and, thus, should be more sensitive to charged particles. In this paper we report [9] the synthesis of a novel monomer, N-allyloxycarbonyl diethanolamine-bis(allyl carbonate) (NADAC) and its subsequent free radical cast polymerization. A co-polymer along with allyl diglycol carbonate (ADC) monomer was also prepared. The kinetics of the polymerization reaction were studied as given in the literature for the allylic monomers like ADC [10].

2. MATERIALS AND METHODS

2.1. Synthesis of the monomer N-allyloxycarbonyl diethanolamine-bis(allyl carbonate) (Scheme 1)

The chemicals used in the reaction were procured from Qualigens (India) and E. Merck (India). Diethanolamine was dried over molecular sieves of 3A grade. Acetone was dried over anhydrous potassium carbonate and then distilled. Pyridine was dried over potassium hydroxide pellets and then distilled.



Scheme 1.

In a three-neck round-bottom flask, equipped with a thermometer, drying tube (CaCl_2) and an addition funnel, dry diethanolamine (6.06 g, 0.0578 mol) and dry acetone (100 ml) were taken. The outer surface of the flask was cooled by artificial circulation of cold methanol, the internal temperature of the reaction mixture was maintained between 0 and 5°C. Allyl chloroformate (21.61 g, 0.1771 mol) and pyridine (13.81 g, 0.1771 mol) were then added simultaneously with stirring. The reaction mixture was then stirred for about 1 h and the contents of the flask were allowed to attain room temperature. The solvent was then removed under reduced pressure at room temperature. The reaction mixture was then suspended in ether (50 ml) and washed with water (4×20 ml) and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure at room temperature. The crude product (weighing 17.50 g) was then vacuum distilled at 180°C and 0.1 mbar pressure. The distilled product weighed 16.50 g (80%, based on diethanolamine).

2.1.1. Spectral characterization of NADAC. IR spectra were recorded on a Shimadzu FT-IR spectrophotometer. ^1H - and ^{13}C -NMR spectra were recorded on a Bruker 300 MHz spectrophotometer. Mass spectra were recorded on QStar XL MS-MS system. IR (neat): 1758 cm^{-1} (s), 1710 cm^{-1} (s), 1655 cm^{-1} (m), 1250 cm^{-1} (s). ^1H -NMR (CDCl_3 , 300 MHz): 3.5 ppm (2H, t), 4.1 ppm (2H, t), 4.5 ppm (2H, t), 5.19 ppm (2H, dd), 5.90 ppm (1H, m). ^{13}C -NMR (CDCl_3 , 75 MHz): 47.47 (t), 65.85 (t), 66.27 (t), 68.45 (t), 117.63 (t), 118.87 (t), 131.35 (d), 154.67 (s), 155.58 (s). MS-ESI ($\text{CH}_3\text{OH} + \text{H}_2\text{O} + \text{CH}_3\text{COONa}$): m/z (amu) 380.12 ($M + \text{Na}^+$), 358.16 ($M + 1$).

2.2. Polymerization of NADAC and co-polymerization of NADAC-ADC

The NADAC monomer, isopropyl peroxydicarbonate (IPP) initiator prepared in our laboratory, highly polished float glass plates, thin teflon sheets (500 μm), polymerization unit (consisting of a Julabo HP F25 programmable bath and polymerization vessel) were used for polymerization. The various steps involved in the polymerization are described below.

2.2.1. Development of constant rate polymerization cycle. As pointed out by Dial *et al.* [10], the allylic polymerization is highly exothermic in nature and the polymerization should be carried carefully and slowly for extended time period. It is also known that the allylic monomers in general and ADC monomer in particular shrink by about 14% of its volume during the process of solid polymer formation. The exotherm and the shrinkage collectively lead to cracking of the films if proper care is not taken. Dial *et al.* [10], after a careful kinetic study, have proposed some kinetic equations by which constant rate polymerization cycle can be defined with a constant rate of catalyst decomposition, as well as monomer conversion, thus resulting in a constant rate of heat evolution. Although Dial *et al.* have

studied this rate of polymerization for a tetra-functional allylic monomer, ADC, we thought of extending their idea to a hexafunctional allylic monomer and mixture of allylic monomers. Thus, the change in monomer concentration and the initiator concentration as a function of time was studied.

The monomer concentration was estimated using the Wij unsaturation analysis procedure, while the initiator concentration was measured by iodometry. A series of test-tubes containing the monomer and the required amount of catalyst were heated at constant temperature at 35°C, 45°C and 55°C, and analyzed for the monomer and catalyst concentration at different time intervals for NADAC monomer and a 1:1 (w/w) mixture of NADAC and ADC monomers as shown in Figs 1 and 2, respectively.

From Figs 1 and 2, it can be seen that the rate of change of monomer concentration was proportional to the rate of change of catalyst concentration. In order to calculate the heating cycle for a constant rate of polymerization, the equations proposed by Dial *et al.*, given below, were solved.

$$K_1 = Z_1 e^{-E_1/RT} \quad (1)$$

$$K_3 = Z_3 e^{-E_3/RT} \quad (2)$$

$$K_3 = Z_3 e^{-E_3/RT} (m_0 - K_4 t) \sqrt{c_0 - \frac{K_4 t}{Z_1 e^{-E_3/RT}}}, \quad (3)$$

where E is the pseudo energy of activation, t is time in h, T is the temperature in K, m_0 is the initial monomer concentration, c_0 is the initial catalyst concentration and K_1 , K_3 , Z_1 and Z_3 are kinetic constants. Using the above equations the constants involved in the Dial equation were found and the values are given in Table 1 for the homo-polymer and the co-polymer, respectively.

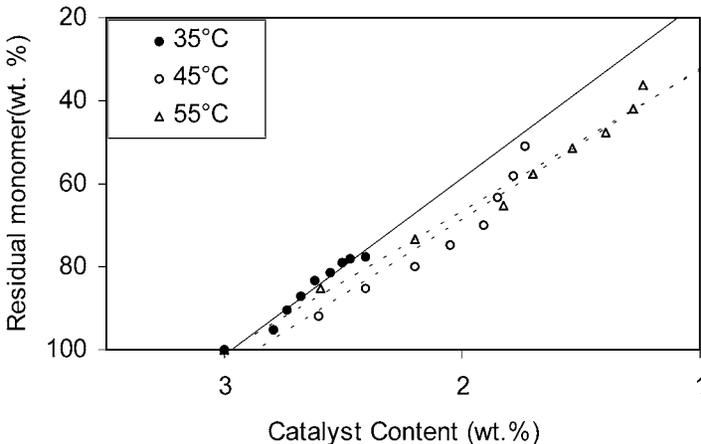


Figure 1. Decomposition of IPP catalyst in NADAC. The straight lines indicate the corresponding least-square fit.

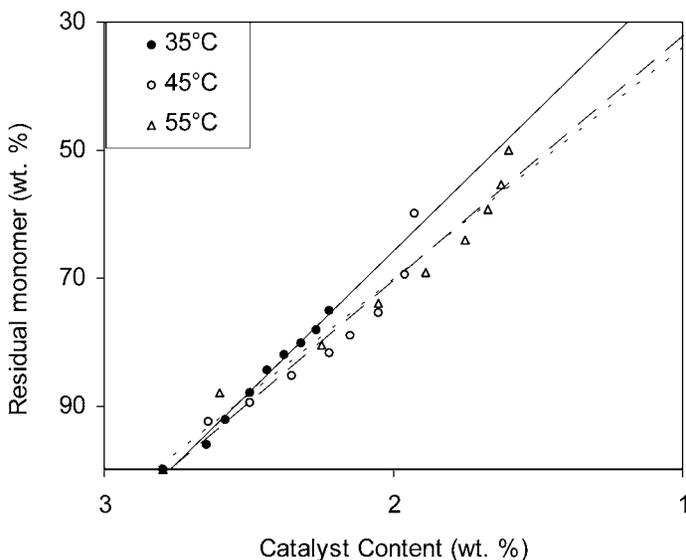


Figure 2. Decomposition of IPP catalyst in NADAC + ADC. The straight lines indicate the corresponding least-square fit.

Table 1.

Constants involved in the Dial equations

Homo-polymer	Co-polymer
$E_1 = -2254.10 \text{ cal}$	$E_1 = -2013.08 \text{ cal}$
$Z_1 = 1.01$	$Z_1 = 1.60$
$E_3 = 18711.57 \text{ cal}$	$E_3 = 16896.54 \text{ cal}$
$Z_3 = 5.2 \times 10^{11}$	$Z_3 = 2.3 \times 10^{10}$

Using these constants in solving the Dial equation (3), the 12 h heating time cycle was obtained as shown in Fig. 3.

In order to check the effectiveness of the heating time cycle obtained as shown in Fig. 3, a series of test tubes containing the catalyzed monomer were placed in the polymerization bath and the % yield of polymer was checked over a period of 12 h. The data obtained are shown in Figs 4 and 5, respectively.

Since Dial *et al.* have proposed polymerisation at a constant rate, a linear correlation is expected between yield of polymer as a function of time. This is supported well by the linear correlation coefficient (R^2) of 1, obtained from calculated yields at a given time interval. If, the same kinetic model is applied to our present polymerisation systems (either NADAC or a mixture of NADAC + ADC), a similar linear relationship can be expected. Since the linear correlation coefficients (R^2) for the yield of polymer as a function of time for these two systems are also close to 1 (0.9953 for homo-polymerisation data and 0.9899 for co-polymerisation data, respectively), it can be said that they obey the same kinetic

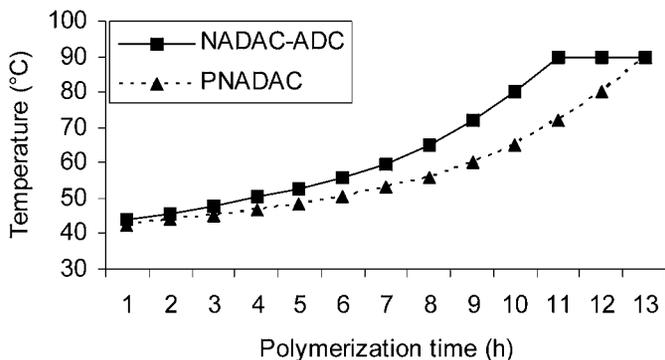


Figure 3. Calculated temperature changes in 12 h time constant rate polymerization cycle for homo-polymerization and co-polymerization.

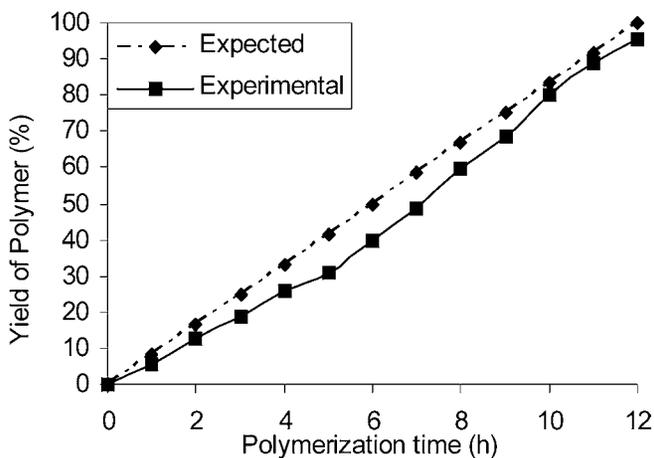


Figure 4. Polymerization of NADAC using a time cycle of 12 h. Catalyst concentration 3.0 wt%.

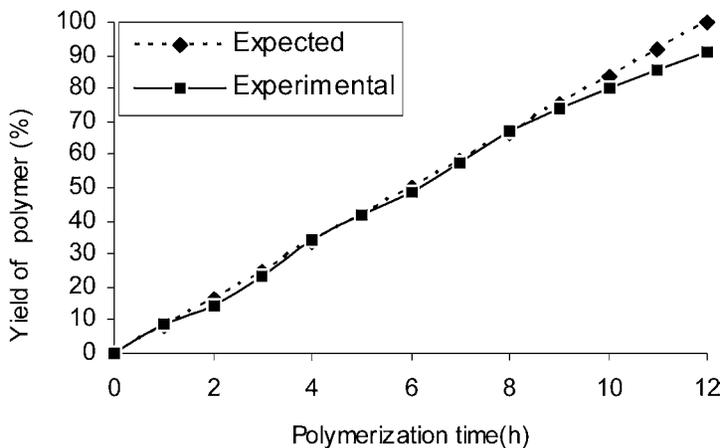


Figure 5. Polymerization of NADAC-ADC in a time cycle of 12 h. Catalyst concentration 3.0 wt%.

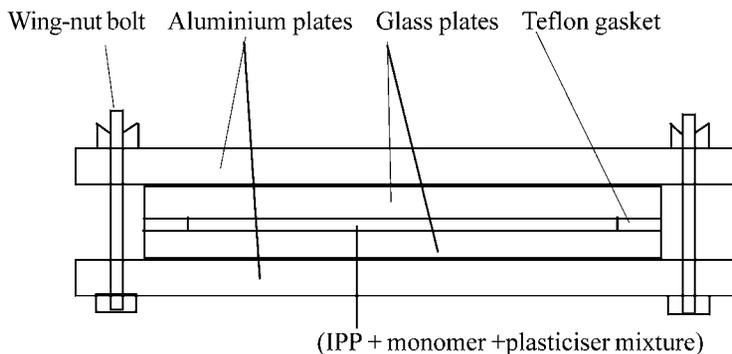


Figure 6. Mold arrangement used for cast polymerisation.

model as proposed by Dial *et al.* However, the calculated and observed sets of data show a slight variation, which is reflected by the average deviation from expected value of -1.79 for homo-polymerisation data and -5.71 for co-polymerisation data. These deviations could be attributed, in general, to experimental errors in estimating monomer/catalyst concentrations titrimetrically and also to efficiency of the electronic temperature controller used for heating purpose. The higher deviation in case of copolymerisation may be due to the fact the kinetic model by Dial *et al.* is applied to a mixture of two different monomers.

2.2.2. Preparation of the mold. A square-shaped gasket of Teflon of outer length 100 mm with an inner window of length 87 mm and thickness of 500 microns with an opening of 2 mm was specially prepared for this purpose. A thin layer of a commercially available pressure-sensitive adhesive was applied to it from both sides and it was sandwiched between two clean float glass plates of size 100 mm \times 100 mm \times 4 mm. Figure 6 shows the design of the mold arrangement used for polymerization.

2.2.3. Preparation of homo-polymer (PNADAC) and co-polymer films by cast polymerization. The monomer was filtered carefully through a G4 sintered crucible to remove any solid impurities and then kept under nitrogen atmosphere to remove any dissolved oxygen which hinders the polymerization process. To the (IPP + monomer + plasticiser mixture) purified monomer was then added the desired concentration of catalyst and dioctyl phthalate (1 wt% of monomer), since it is known that the surface of the chemically etched film remains transparent when the dioctyl phthalate in 1–3 wt% concentration is added prior to the polymerization. The monomer along with the initiator was then injected into the glass mold through a slot prepared in the teflon gasket previously. Care was taken to see that no air bubbles are trapped inside the liquid monomer film during the injection into the mold. The entire assembly was tightened between two flat aluminium plates and pressurized using wing-nut bolt arrangement present at the corners of the mold. The mold was then placed vertically in the polymerization bath and heated as per

the heating profiles mentioned previously. In order to avoid cracking of the films due to the shrinkage which occurs during polymerization the molds were periodically tightened. After the end of heating cycle the mold was allowed to cool on its own till it reaches room temperature and then opened. A clear transparent film of $7.5 \text{ cm} \times 7.5 \text{ cm}$ in size and thickness of $650 \pm 10 \mu\text{m}$ was obtained which was then cut into small pieces of $1 \text{ cm} \times 1 \text{ cm}$ size and tested for SSNTD applications.

3. TESTING OF PNADAC AND CO-POLYMER FILMS FOR SSNTD APPLICATION

Small pieces ($1 \text{ cm} \times 1 \text{ cm}$) of the films prepared were then exposed to a electro-deposited ^{239}Pu alpha particle source in close contact in order to record the autoradiograph of the source on the film, also the fission fragment tracks were recorded by exposing to electro-deposited ^{252}Cf source. The films were then studied for their sensitivity for the alpha particles, Sensitivity (S) was found by measuring the track diameter of alpha particles (D_a), the track diameter of fission fragments (D_f) and by using the following equation [11]:

$$S = (1 + (D_a/D_f)^2)/(1 - (D_a/D_f)^2) \quad (4)$$

The films were chemically etched in aqueous sodium hydroxide solution of different concentration and at different temperature. The etching conditions which would reveal the tracks in about approx. 6–7 h were chosen in order to have a rapid analysis of the films. Thus an aqueous sodium hydroxide concentration of 6 M and temperatures of 80 and 75°C were found to be optimal for the homo-polymer and the co-polymer, respectively. The sensitivity of the homo-polymer as well as the co-polymer was found to be higher than that obtained for CR-39. The films were also tested for their alpha track registration efficiency, the results were compared with the CR-39 (Pershore Moldings) film. The results are given in Table 2. It was found that good alpha tracks were developed within 2, 8 and 4 h of etching time in case of CR-39, PNADAC and NADAC-ADC co-polymer, respectively, whereas the sensitivity of the materials reached an optimum value after 4, 11 and 7 h of

Table 2.

Comparison of track detection characteristics of the novel polymers with CR-39

Polymer	Etching conditions	Track detection efficiency		Sensitivity
		Background tracks/cm ²	Alpha tracks/cm ²	
CR-39	6 M NaOH, 70°C	258	25 890	1.18
PNADAC	6 M NaOH, 80°C	220	26 814	1.35
NADAC-ADC	6 M NaOH, 75°C	409	26 789	1.60

Track detection efficiency: exposure to ^{239}Pu (264 684 dpm) at 2 cm from the source for 3 min. Sensitivity: exposure to ^{252}Cf (300 dpm) at 3 cm from the source for 5 h in vacuum (0.1 mbar).

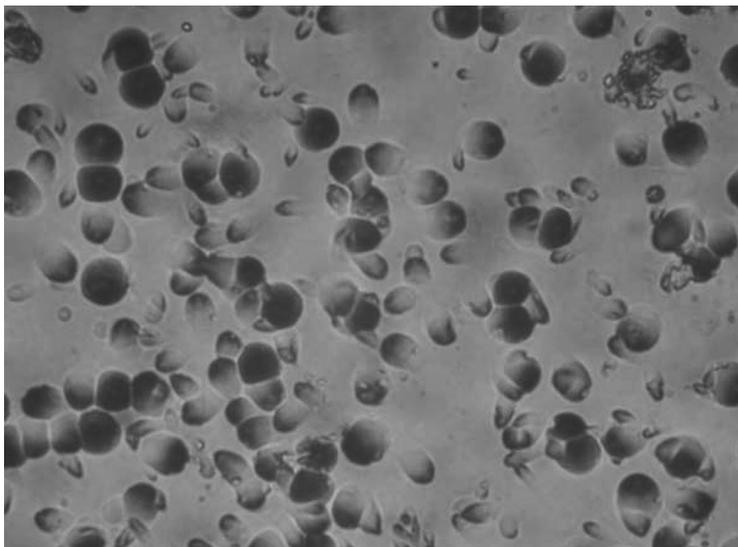


Figure 7. A photomicrograph of a ^{239}Pu alpha source autoradiograph in PNADAC film. Magnification $160\times$.

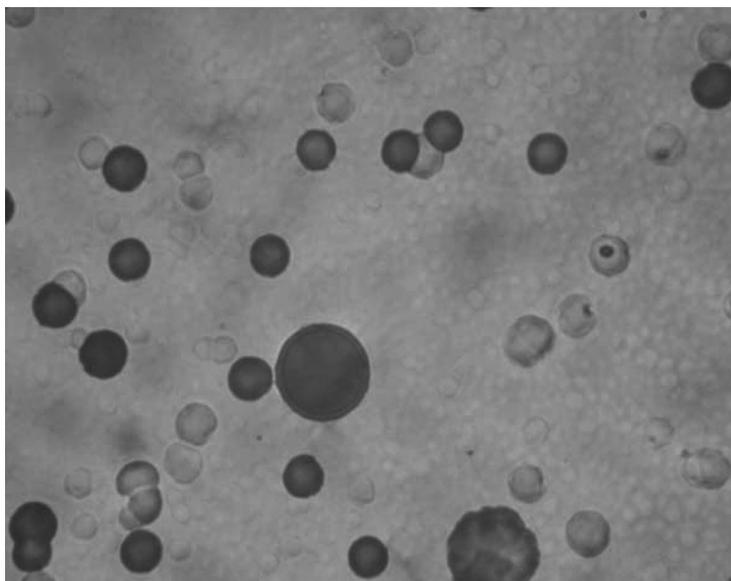


Figure 8. A photomicrograph of ^{252}Cf fission fragments and alpha particles in co-polymer film. Magnification $160\times$.

etching time under given conditions for CR-39, PNADAC and NADAC-ADC co-polymer, respectively. It can be seen that the background tracks registered by the co-polymer are slightly on the higher side, the background tracks can be attributed to the radiation sources available in the environment, like radon, thorium, etc., and also

to the matrix faults arising in the polymer which due to fine dust particles, bubbles, appear as particle tracks. From the data it is shown that the alpha track registration efficiency for the homo-polymer and the co-polymer are comparable to that of the commercially available CR-39 track detector. The photomicrographs of the tracks of alpha particles and fission fragments formed in the homo- and co-polymer are shown in Figs 7 and 8.

4. CONCLUSIONS

We have designed a new monomer for preparing more sensitive materials to be used as SSNTDs. The homo- and co-polymer are found to be more sensitive for detection of alpha particles and fission fragments than the presently available SSNTD materials. The new materials are found to be favourable in all the requirements of SSNTD materials, such as transparency, track development upon chemical etching with alkali metal hydroxides, viewing of the tracks under optical microscope and stability of the materials. The polymerization profile of this hexafunctional allylic monomer is in accordance with the kinetic model proposed by Dial *et al.* [10].

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