Poly(triallyl phosphate) and its copolymers with allyl diglycol carbonate as solid state nuclear track detectors.

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ABSTRACT
This paper describes the design and development of new polymers for solid state nuclear track detection. A monomer triallyl phosphate (TAP) has been synthesized and cast homopolymerized with allyl diglycol carbonate (ADC) to get transparent thin films of poly(triallyl phosphate) (PTAP) and poly(TAP-co-ADC) polymers respectively, which were successfully explored for the first time for detection of alpha particles and fission fragments. The polymerization kinetics studies were carried out to generate constant rate polymerization profile for TAP and TAP: ADC monomer mixture. Poly(TAP-co-ADC) copolymer in 3:7 wt./wt. ratio showed better radiation sensitivity as compared to indigenously prepared PADC and commercially available CR-39 detectors.

KEYWORDS
solid state nuclear track detection (SSNTD); triallyl phosphate (TAP); polytriallyl phosphate (PTAP); allyl diglycol carbonate (ADC); homopolymerization; copolymerization; nuclear track detectors

1. Introduction
The discovery of latent tracks in the LiF crystal in 1958, by D. A. Young [1] lead to the development of a new field called solid state nuclear track detection (SSNTD). Many materials including minerals, glasses and a variety of plastics have been tested for track revelation studies.[2–4] Polymers like Cellulose nitrate (LR-115) and Bisphenol-A polycarbonate (Lexan) and poly(allyl diglycol carbonate) (CR-39) are preferred for track detection. In 1966, phosphate glass prepared by Toshiba Co. Ltd., Japan was used as track detector for the first time by Becker [5] for thermal and fast neutron dosimetry in mixed radiation field. Various other sensitive phosphate glass detectors have been reported.[6–8] Further, Barium phosphate BP-1 glass detector was described by R. Bonetti et al. due to its high sensitivity compared to some polymers.[9] In 1997, Bonetti [10] and co-workers have calibrated LG 750 phosphate glass with heavy ion beams, as it is known previously that LG750 phosphate glass is suitable to detect cluster radioactivity because of its very high tolerance of alpha dose. [11] However, glasses generally have poor radiation sensitivity compared to many plastics. In year 1978, Cartwright et al.,[12] made use of CR-39 polycarbonate for the first time as SSNTD and found to be best for track detection with high radiation sensitivity as compared to all other track detectors. For past more than three decades, the scientists are using CR-39 as sole polymeric material for nuclear track detection studies.

In the recent past, we have developed various novel polymeric materials as nuclear track detectors.[13–18] Interestingly, no polymeric nuclear track detectors containing phosphate functionality are reported so far. We, now report for the first time such phosphate and phosphate-carbonate containing polymeric detectors for nuclear track detection. We have earlier studied the use of branched monomers like Poly-[N-allyloxy carbonyl diethanolamine-bis(allylcarbonate)] (NADAC),[13] Tris-(2,4-dioxa-3-oxohept-6-en-1-yl)nitromethane, (TDONM),[16] pentaerythritol tetrakis(allyl carbonate) (PETAC) [17] and observed that the polymers derived from them tend to show better radiation sensitivity mainly owing to formation of a denser cross-linked network. We, therefore, decided to use a hexafunctional branched monomer like triallyl phosphate in our present study.

Triallyl phosphate monomer has been synthesized [19] and cast polymerized into thin transparent films using isopropyl peroxydicarbonate (IPP) initiator and dioctyl phthalate (DOP) plasticizer. TAP monomer was also copolymerized with ADC monomer using IPP initiator and DOP as plasticizer. The kinetics of the polymerization reaction was studied by extending polymerization kinetics model developed by Dial et al. [20] for allylic monomers like ADC. Alpha sensitivity of the copolymer Poly(TAP-co-ADC) was determined and compared with indigenously prepared PADC and commercially available CR-39.
2. Materials and methods

All the starting materials and solvents used for the synthesis were Analytical Reagent grade (AR grade). Solvents like toluene, acetone were initially distilled and dried before use. AR grade phosphorus oxy chloride (POCl₃) was obtained from Loba chemie Pvt. Ltd. and used as received. Allyl alcohol (AR grade, Spectrochem Pvt. Ltd) was used directly without further purification. Triethyl amine and pyridine (AR grade, Spectrochem Pvt. Ltd.) were dried before use. Allyl chloroformate, diethylene glycol (AR grade, Spectrochem Pvt. Ltd.) were used as received. Infrared spectra were recorded on a Shimadzu FT-IR spectrophotometer and NMR spectra were recorded on 400-MHz NMR spectrometer (Bruker Avance 400 instrument) at Goa University. Photographs of the tracks were recorded using Tucsen ISH500 Camera attachment and track diameters were determined using its imaging software called IS Capture.

2.1. Synthesis and polymerization of triallyl phosphate (TAP) monomer

The TAP monomer has been synthesized by the method of Whitehill and Baker [19] from phosphoryl oxy chloride on reaction with allyl alcohol at low temperature in a one-step process. Initially, 23.08 g (0.398moles) of allyl alcohol with 70 mL of toluene was charged into the three-necked round-bottom flask fitted with mechanical overhead stirrer and two pressure equalizing funnels. The whole assembly was placed in a Julabo cryostat which was maintained at −60 °C. After 15 min of attaining the desired temperature 17.019 g (0.111 mol) of phosphoryl oxy chloride and 34.91 g (0.3449 mol) of triethyl amine were added dropwise through pressure equalizing funnel in such a way that the ratio of the two reagents was 1:3, respectively. Addition was carried out for a period of 3 h. Once the addition was complete, reaction mixture was stirred for 12 h in ice salt bath. After monitoring the reaction using TLC, the solid mass formed in the reaction was filtered and was extracted with 50 ml of dichloromethane 4 times. Then combined organic solvent containing product was washed with brine and finally triallyl phosphate was vacuum distilled at 100 °C and 0.5 mm of mercury. The yield of triallyl phosphate (TAP) monomer was characterized by infrared spectrum and 1H, 13C NMR spectra.

FTIR (neat): 1150 cm⁻¹ (s), 900–1050 cm⁻¹ (s), 3086.11 cm⁻¹ (s). 1H-NMR (CDCl₃, 400 MHz): 5.828–5.924 ppm (3H, m), 5.282–5.325 ppm (3H, d), 5.177–5.203 ppm (3H, d), 4.468–4.503 ppm (6H, t). 13C-NMR (CDCl₃, MHz): 132.29 (t), 118.50 (t), 68.10 (t). Its unsaturation analysis was carried out using Wij’s method and unsaturation index was observed to be 3. The Scheme 1 depicts the synthesis, homopolymerization of TAP and copolymerization of TAP with ADC using initiator and plasticizer.

2.2. Synthesis of allyl diglycol carbonate

The synthesis of allyl diglycol carbonate (ADC) was carried out by transesterification process developed and patented by AAA Mascarenhas et al. in our laboratory. This involves reaction of diethylene glycol with diallyl carbonate (DAC) in presence of catalytic base like KOH and phase transfer catalyst (PTC). [21] The monomer so prepared was cast polymerized using (3.3 wt.%) IPP initiator and 0.1% DOP plasticizer to produce indigenous PADC films.

2.3. Preparation of polymer films

2.3.1. Designing mould for cast-polymerization

The polymer films of triallyl phosphate are prepared by free radical polymerization using initiator like benzoyl peroxide, isopropylperoxy dicarbonate (IPP) and dioctyl phthalate as plasticizer. For casting polymer films, a mould is required. The design of mould should be such that during injection of any liquid monomer into the mould, no air bubble should be trapped inside as it is well known that trapped air bubble leads to colouration of polymer film and also cracking of film occurs. So it is very important that the shape of the polymerization mould should be proper. Earlier, we have used a mould assembled by sandwiching square-shaped wrinkle-free Teflon gasket of 1 inch width and 500–600 μ thickness between two clean dust-free Schott glass plates.[22] To overcome trapping of air bubble we suggested modification of the shape of Teflon gasket by keeping tapering at the opening as shown in Figure 1.

2.3.2. Preparation of PTAP and poly(TAP-co-ADC) SSNTD films by cast polymerization

Triallyl phosphate is filtered through 0.45-μ Ultipor N66 Nylon membrane (make PALL Life Sciences) followed by bubbling nitrogen gas for period of 30 min. The calculated amount of the monomer is mixed homogenously with optimized quantity of initiator (3.3 wt.%) isopropyl peroxy dicarbonate IPP and 0.1 wt.% of dioctyl phthalate plasticizer. This mixture is injected into the mould with help of syringe pump and mould is sealed properly with Teflon stopper. The mould is then placed into the polymerization bath. The polymerization is carried out using 12 h constant rate polymerization temperature–time profile generated for TAP and its copolymer with ADC. Heating is controlled using programmable Julabo F2SHL bath. After completion of 12 h of polymerization, the mould in bath is cooled naturally for period of 12–14 h. The per cent polymerization
of the polymer films is experimentally determined using Wij’s method for unsaturation analysis.\[23\]

Homopolymer and different copolymers with allyl diglycol carbonate prepared above were tested for track detection characteristics. All detector films were exposed to $^{239}\text{Pu}$ and $^{252}\text{Cf}$ sources and etched chemically using 7 N NaOH at 70 °C.

### 3. Kinetic studies for development of constant rate polymerization cycle of TAP and (37 ratio) of TAP-ADC

It is a known fact that allylic free radical polymerization is an exothermic process and due to which cracking of polymer film occurs while casting thin films (below 1 mm thickness). Also volume shrinkage of monomer up to 14% occurs during this process. So during polymerization, it becomes necessary to control the heat evolved and to carry out polymerization at low temperature over longer period of time. In order to overcome such problems faced during allylic polymerization to cast thin polymer films, Dial et al. had suggested use of constant rate polymerization profile based on the following kinetic equation.

$$K_4 = Z_1 e^{-\frac{E_1}{R T}} \left(M_0 - K_4 t\right) \sqrt{C_0 - \frac{K_4 t}{Z_3 e^{-\frac{E_3}{R T}}}}$$

Where, $K_4$ is rate of polymerization, $Z_1$ and $Z_3$ are Arrhenius constants, $E_1$ and $E_3$ are energies of activations, $M_0$ & $C_0$ are initial concentrations of monomer & initiator respectively, $R$ is gas constant. Temperature $T$ at a given time $t$ is calculated using this equation. We have already extended this method successfully to many other allylic monomers and devised constant rate polymerization profiles for such monomers to cast thin (0.5–0.7 mm) detector films. Constant rate polymerization results in a smooth evolution of heat and gives a polymer with more uniform bulk properties. This methodology was extended by us to develop constant rate polymerization profile for hexafunctional allylic monomer containing phosphate functionalities i.e. for TAP monomer. Also for a mixture of ADC and TAP constant rate polymerization cycle was developed. Starting with known concentrations of monomer and initiator, we determined change in their concentrations as a function of time. Residual monomer concentration was determined using ICl (Wij method) and peroxide concentration was determined by iodometric titration. A series of test tubes containing mixture of monomer and IPP initiator (3.3% by weight) were taken, and flushed with nitrogen gas and tightly sealed. Three such separate sets were placed in the water bath and after certain period of time each test tube was analysed for its peroxide concentration and residual monomer concentration by iodometric titration. This way, the residual monomer concentration and peroxide concentration were determined as a function of time at 35, 45 and 55 °C. Figure 2 and 3(a) depicts the nature of decomposition of initiator in the monomer at three different temperatures. Using the kinetics constants calculated using the graphs; the parameters ($E_1$, $Z_1$, $E_3$ and $Z_3$) involved in the Dial equation were calculated and are given in Table 1 for both homopolymer and copolymer. The constant rate polymerization cycles for homo and copolymerization for 12 h and 24 h were calculated as shown in Figure 4(a) using the above said Dial methodology. To test the effectiveness of the calculated polymerization cycle, a correlation study was performed \[24\] as shown in the Figure 5. The correlation coefficient for 24 h PTAP constant rate polymerization cycle was found out to be 0.9980 but it may be noted that for the first 12 h, the linear correlation coefficient was 0.9998. When correlation studies were carried out for 12-h constant rate polymerization cycle for PTAP, linear correlation coefficient was 0.9931. As polymerization proceeds, more and more three dimensionally cross-linked polymer is formed which is increasingly insoluble in the solvent used for Wij method. This might result in lesser estimation of non-polymerized
polymerization process. Kinetic study of TAP-ADC mixture using benzoyl peroxide (BP) initiator at 55, 65 and 75 °C was also carried out in similar fashion to generate 12-h constant rate polymerization cycle shown in Figure 4(b). Figure 3(b)

C=C bonds which might remain trapped in the rigid polymer structure. The constant rate polymerization cycle for poly(TAP-co-ADC), is supported well by the linear correlation coefficient ($R^2$) of 0.9989. This clearly indicates that the polymerization cycle generated by us for both homo and copolymer is in good agreement with the kinetic model as proposed by Dial and co-workers and can be used for cast polymerization.
the use of IPP for polymerization as it leads to good-quality detector films. Also the background tracks like features are lesser in case of films prepared using IPP as compared to that using BP.

### 3.1. Charged particle detection characteristics of PTAP and Poly(TAP-co-ADC) polymeric films

By using the generated constant rate polymerization cycle, homopolymer and copolymers were prepared in different...
weight ratios of ADC and TAP. Preliminary testing of the same was carried out for track detection studies. Initially, time required for development of alpha and fission fragments’ tracks in the prepared polymeric films was determined and alpha sensitivity [16] of the films was calculated and is given in Table 2.

Hardly few tracks are shown by the homopolymer PTAP material. The bond energy data indicate that the P–O bond is stronger than C–O or N–O bonds but the P=O bond is relatively weaker than C=O. It is also known that the thermal and hydrolytic stability of P=O is more as compared to P=S & P=Se bonds.[25] Oxygen is more electronegative than phosphorus and the stability of P=O bond may be expected to depend upon the other substituents attached to phosphorous atom. In case of triallyl phosphate, due to presence of three electronegative oxygen atoms attached to the phosphorous, the P=O bond is expected to be shorter which results in its increased bond strength. Although, the bond energy of P=O bond is lesser than that of C=O bond, P=O bond in homopolymer PTAP may be expected to be strong enough to resist the alkaline hydrolysis during chemical etching which is well supported by its lower bulk etch rates (about 0.008 μ/h) compared to that of PADC (0.016 μ/h). It is also possible that lone pairs on oxygen of the phosphate group are held relatively tightly, so that ejection of these electrons (i.e. delta rays which cleave surrounding bonds thereby forming tracks) is probably not sufficient, resulting in the formation of very less number of tracks when compared with PADC which has a carbonate link. We have noted that PTAP exposed to 239Pu alpha particles at a distance of three centimetres from source hardly shows any alpha tracks when compared with PADC detector (which shows almost expected number of alpha tracks) observed under identical experimental conditions.

The sensitivity measurements were carried out by exposing each piece of detector film to 252Cf source at a distance of 5 cm from radiation source under vacuum (0.2 mm of Hg) for 8 h and followed by chemical etching. All films were etched in 7 N NaOH solution at 70 °C. Further, the alpha track registration efficiency [18] of the copolymer, Poly(TAP-co-ADC, 3:7 wt./wt.) was compared with that of indigenously prepared PADC film and commercially available CR-39. Table 3 shows the comparison of alpha track efficiency and sensitivity of novel copolymer 3:7 poly(TAP-co-ADC) with indigenously prepared PADC and CR-39. Alpha tracks and fission fragments in 3:7 (w/w) poly(TAP-co-ADC) could be viewed in Figures 6 and 7 which were independently exposed to alpha source 239Pu at 1 mm for 2 min and to fission fragments source 252Cf at 1 mm for 2 h. Both films were etched in 7 N NaOH at 70 °C for 2.5 h. Figure 7 depicts alpha and fission tracks in poly(TAP-co-ADC, 3:7wt./wt.) on etching for 2 h in 7 N NaOH at 70 °C which was initially exposed to 252Cf source at a height of 5 cm, under 0.2 mm of Hg vacuum for 8 h.

4. Conclusions

Development of novel polymeric track detector materials containing phosphate functionality is reported for the first time. Triallyl phosphate monomer synthesized has been cast polymerized to PTAP homopolymer and copolymerized with ADC to generate novel poly(TAP-co-ADC) copolymer for nuclear track detection applications. The constant rate polymerization cycle has been developed for both homopolymer and copolymer following the Dial’s methodology. Further, both the homopolymer and copolymer films have been tested for the detection of alpha as well as fission fragments. Poly(TAP-co-ADC) film with 3:7 ratio found out to be more sensitive as compared to indigenously prepared PADC and CR-39. Alpha tracks and fission fragments in 3:7 (w/w) poly(TAP-co-ADC) could be viewed in Figures 6 and 7 which were independently exposed to alpha source 239Pu at 1 mm for 2 min and to fission fragments source 252Cf at 1 mm for 2 h. Both films were etched in 7 N NaOH at 70 °C for 2.5 h. Figure 7 depicts alpha and fission tracks in poly(TAP-co-ADC, 3:7wt./wt.) on etching for 2 h in 7 N NaOH at 70 °C which was initially exposed to 252Cf source at a height of 5 cm, under 0.2 mm of Hg vacuum for 8 h.

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No potential conflict of interest was reported by the authors.

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