GENERAL REMARKS

- Commercial reagents were used without further purification.
- Solvents were distilled prior to use and dried whenever necessary using standard procedures.
- Petroleum ether refers to the hydrocarbon fraction collected in the boiling range 60-80 °C.
- Thin layer chromatography (TLC) was carried out on silica gel 60 F254 aluminium plates purchased from Merck.
- Chromatographic purification was conducted by column chromatography using silica gel (60-120 mesh size) or by flash chromatography using silica gel (230-400 mesh size) on Combiflash Companion instrument.
- All the melting points and boiling points were recorded using Thiele's tube and are uncorrected.
- The compounds numbers, figure numbers, scheme numbers and reference numbers are referred to the particular chapter.
- IR spectra were recorded on Shimadzu FT-IR spectrophotometer.
- ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on Bruker AVANCE 400 MHz instrument and the multiplicities of carbon signals were obtained from DEPT experiment.
- High-resolution mass spectra (HRMS) were recorded on a MicroMass ES-QTOF Mass spectrometer (at IISc. Bangalore).
- Gas Chromatograph was recorded on Nucon 5700 Gas Chromatographer using capillary column.
- Optical glass plates from Schott, Germany and Teflon^{TM} sheets were used for preparation of polymer molds. Polymerization was carried using a polymerization bath controlled using microprocessor-based electronic temperature controller F25 HP from M/s Julabo, Germany.

ABBREVIATIONS

1. General Abbreviations

aq.	Aqueous	Equiv.	Equivalent
b.p.	Boiling point	*cat.*	Catalytic
conc.	Concentrated	*TLC / tlc*	Thin layer chromatography
dil.	Dilute	*atm.*	Atmospheric
Eq.	Equation/s	RT / rt	Room temperature
fig.	Figure	sat.	Saturated
g	Gram/s	*et al.*	Et alia (and others)
h	Hour/s	*psi*	Pounds per square inch
hv	Irradiation	*MS*	Molecular sieves
lit.	Literature	*p*	Para
m.p.	Melting point	Expt.	Experiment
mg	Milligram/s	Temp.	Temperature
mL	Millilitre	anhyd.	Anhydrous
mmol	Millimol	*Calcd.*	Calculated
Min.	Minute/s	°C	Degree Celcius
%	Percentage	DTD	Dielectric track detectors
w/w	weight by weight	EM	Electron microscope
sec	Second/s	V_t	Track etch rate
DP	Degree of polymerization	θc	Critical angle of etching
CE	Chemical etching	c	Velocity of light
ECE	Electrochemical etching	m	Mass of the particle
OM	Optical microscope	Tg	Glass transition temperature
V_b	Bulk etch rate	V	Velocity of charged particle
S	Sensitivity		

2. Spectroscopic Abbreviations

δ	Delta (Chemical shift in ppm)	*m/z*	Mass to charge ratio
$CDCl_3$	Deuterated chloroform	dd	Doublet of doublet
DMSO-d_6	Deuterated dimethyl sulfoxide	td	Triplet of a doublet
DEPT	Distortionless Enhancement by Polarization Transfer	HRMS	High Resolution Mass Spectrum
cm^{-1}	Frequency in wave number	t	Triplet
$\tilde{\nu}$	Frequency maximum	d	Doublet
Hz	Hertz	br	Broad
HPLC	High Performance Liquid Chromatography	Cq	Quaternary carbon
IR	Infrared	s	Singlet
MHz	Megahertz	*J*	Coupling constant
NMR	Nuclear magnetic resonance	m	Multiplet
ppm	Parts per million	M^+	Molecular ion
UV	Ultra violet	q	Quartet

3. Compound Abbreviations

AA	Allyl alcohol	ADC	Allyl diglycol carbonate
ATC	Allyl thiodiglycol carbonate	ADS	Allyl diglycol sulphite
SDAC	2,2'-sulfonyldiethanol bis(allyl carbonate)	PEBDP	Pentaerythrityl bis (diallylphosphoramidate)
BP	Benzoyl peroxide	CN	Nitocellulose (cellulose nitrate)
CHPC	Cyclohexyl peroxydicarbonate	DEG	Diethylene glycol
CR-39	ADC polymer (Trademark of PPG Industries, UK)	DEAS	Diethylene glycol bis(ally1 sulfonate)
DAC	Diallyl carbonate	DAS	DiaIly1 sulphite
DVS	Divinyl sulfone	DOP	Dioctyl phthalate
IPA	Isopropyl alcohol	IPP	Isopropylperoxydicarbonate
LR-115	(Trademark) CN SSNTD film manufactured by Kodak Pathe, France	NADAC	N-(Allyloxycarbonyl) diethanol amine bis(ally1 carbonate)
NAAAC	N-Allyloxycarbonyl ammediol bis(allyl carbonate)	PETAC	Pentaerythritol tetrakis(ally1 carbonate)
DMPDDP	2,2-dimethylpropan-1,3-diyl diallylphosphoramidate	PeAC	Pentanediol bis(ally1 carbonate)
SR-86(10)	Copolymer of CR-39:DEAS 9:1 w/w	SR-86(20)	Copolymer of CR-39:DEAS 8:2 w/w
PC	Polycarbonate	BP-1	Barium phosphate glass
PET	Polyethylene terephthalate	PP	Polypropylene
TBPB	t-butyl peroxy benzoate	AIBN	Azobisisobutyronitrile
SSNTD	Solid state nuclear track detection	SSNTD's	Solid State Nuclear Track detectors
TAP	Triallyl phosphate		

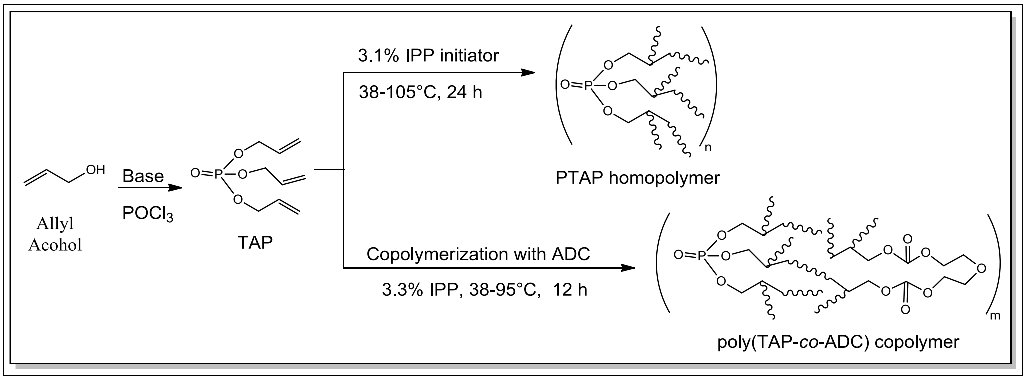
ABSRACT OF THESIS

For last five decades, Solid State Nuclear Track Detection (SSNTD) technique has developed an immense interest in many fields of science and technology. The disciplines where track detectors are frequently in use are nuclear physics, nuclear imaging, nuclear technology, space physics, microanalysis, mine safety, environmental research, uranium prospecting, biomedical sciences, for cancer treatment by radiation therapy (BNCT), material sciences, and geological sciences which have made this technique more versatile and popular. Commercial CR-39 polymeric detector is the only detector vastly used for neutron dosimetry and dosimetry of heavy ions and radon. Although materials like bisphenol-A polycarbonate (Lexan/Makrofol), nitrocellulose (LR-115) etc. could be used as charged particle detectors; there is no replacement available so far for the PADC detector due to its superiority in many aspects. During the course of research work, our efforts were directed towards designing and developing more efficient track detectors than CR-39.

The thesis entitled "Synthesis of allylic monomers and polymers containing Sulphur and Phosphorus functionalities for Solid State Nuclear Track Detection" comprises of four chapters.

The ***first chapter*** incorporates the introduction and literature review about SSNTD technique. In this chapter origin of radiation, its hazardous effects and different types of radiation detectors used earlier for radiation detection have been discussed. Also advantages, important features and applications of SSNTD technique have been discussed here.

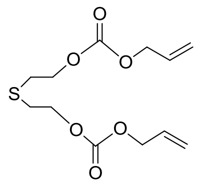
The ***second chapter*** includes the designing and development of phosphorus containing polymers for SSNTD applications. Here, we considered development of some phosphate, phosphoramidate containing monomers/ polymers for our study. Out of which triallyl phosphate (TAP) has been homopolymerized and also copolymerized with allyl diglycol carbonate to generate polymeric film detectors (Scheme 1).



Scheme 1

Initial studies of PTAP and poly (TAP-*co*-ADC) as track detectors were carried out. PTAP homopolymer hardly detected any alpha tracks. But, Poly (TAP-*co*-ADC) polymeric film revealed tracks and has been optimized as per the protocol proposed for systematic development of polymeric track detectors. The alpha sensitivity as well as alpha track detection efficiency of optimised poly (TAP-*co*-ADC) polymer were compared with commercial CR-39 and indigenously prepared PADC detectors. Copolymers poly (TAP-*co*-PETAC) and poly (TAP-*co*-NADAC) have also been prepared and successfully tested for nuclear track detection.

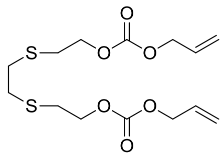
The ***third chapter*** describes design and development of sulfur containing monomers/ polymers for SSNTD applications. Here we have reported the synthesis of monomers containing sulfide, sulfoxide, sulfonamide, and sulfone functionalities. Attempts were made to cast polymerize the synthesized monomers.



Allyl thiodiglycol carbonate (ATC)

CAS No. 128809-87-0

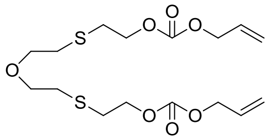
(M1)



3,6-dithiaoctan-1,8-diol bis (allyl carbonate)

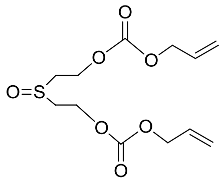
CAS No. 128809-89-2

(M2)



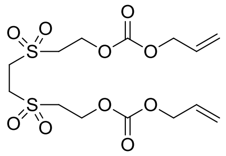
5,5'-oxybis(3-thiapentan-1-ol) bis(allyl carbonate) **OR** 3,9-dithia-6-oxa-undecane-1,11-diol bis(allyl carbonate)

(M3)



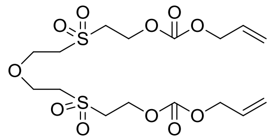
2,2'-sulfinyldiethanol bis (allyl carbonate)

(M4)



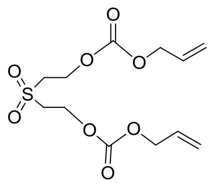
2,2'-(ethane-1,2-diyldisulfonyl)diethanol bis (allyl carbonate)

(M5)



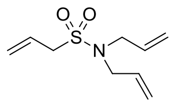
2,2'-(3-oxapentane-1,5-diyldisulfonyl)diethanol bis (allyl carbonate)

(M6)



2,2'-sulfonyldiethanol bis(allyl carbonate) (SDAC)

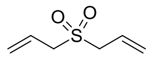
(M7)*



N,*N*-diallylprop-2-ene-1-sulfonamide

CAS No. 1852256-21-3

(M8)



Allyl Sulfone

CAS No. 16841-48-8

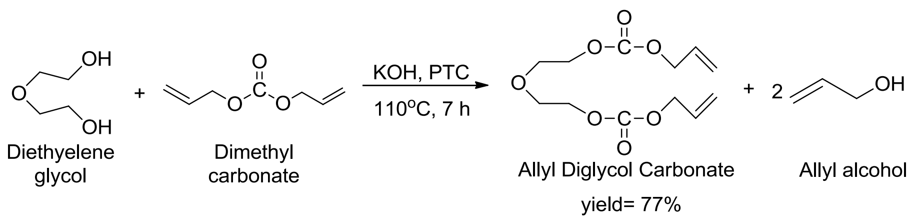
(M9)

*Note: Compound **M7** has also been referred as Allyl Thiodiglycol Sulfone Carbonate (ATSC) by us in some other communications.

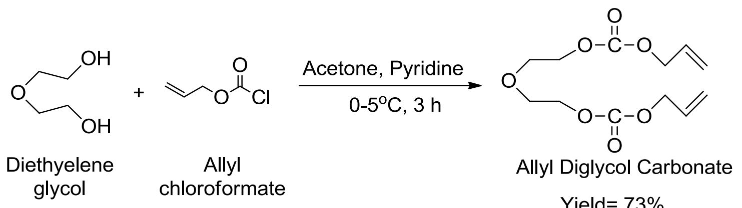
Out of several monomers, process of casting detector films from 2,2'-sulfonyldiethanol bis(allyl carbonate) (SDAC) monomer was optimized as per the protocol mentioned above. Polymerization kinetics for PSDAC as well as poly (SDAC-*co*-ADC) was studied to generate 12 h constant rate polymerization profile. Time required for track development, alpha sensitivity, alpha track efficiency, alpha to fission fragment ratio as well as neutron sensitivity of homopolymer PATSC and copolymers poly (SDAC-*co*-ADC) were studied. PSDAC and poly (SDAC-*co*-ADC) detectors showed alpha sensitivity values of 1.95 & 2.75 respectively which is higher than that of CR-39 (1.28). These new polymers could also detect recoil proton tracks from fast neutrons. It was interesting to note that the PATSC and poly (SDAC-*co*-

ADC) detectors reveal alpha, fission or proton tracks within a few minutes whereas CR-39 requires a few hours for the same.

The ***fourth chapter*** deals with the development of PADC polymeric track detector for the personnel neutron dosimetric analysis and an attempt towards its commercialization. Although PADC detectors are widely used for monitoring thermal neutron doses due to its sensitivity towards neutrons through (n, p) reactions, and excellent optical properties but, these detectors are not manufactured in India and are obtained only through import procedure (i.e. commercial CR-39 detectors). So with this view in mind, we have successfully scaled up the synthetic process to prepare ADC monomer and cast polymerized ADC monomer to obtain polymeric films of size upto 10” x 10”. Synthesis of ADC was carried out using two methods i.e. transesterification process (scheme 2) and condensation process (scheme 3).



Scheme 2



Scheme 3

Process to cast PADC sheets of 10” X 10” was developed and the PADC detectors were tested for the dosimetric parameters such as minimum dose limit (MDL value), sensitivity and signal to noise ratio. Based on these parameters, improvements in polymerization process were carried out to develop a dosimetry grade PADC detector sheet.

LIST OF PUBLICATIONS

International peer reviewed journal publications:

1. R. Pal, V. S. Nadkarni, **D. G. Naik**, *et. al.*, Development and dosimetric characterization of indigenous PADC for personnel neutron dosimetry. Nuclear technology and radiation protection, 30(3), 175-187, **2015**. http://dx.doi.org/10.2298/NTRP1503175P
2. **D. G. Naik** and V. S. Nadkarni, Poly (triallyl phosphate) and its copolymers with allyl diglycol carbonate as Solid State Nuclear Track detectors. Designed monomers and polymers, 19(7), 643-649, **2016**. http://dx.doi.org/10.1080/15685551.2016.1187445
3. **D. G. Naik** and V. S. Nadkarni, Poly (sulfone-carbonate) detectors for rapid detection of nuclear tracks by chemical etching (*manuscript under communication).*
4. **D. G. Naik** and V. S. Nadkarni, Polyphosphates and poly (phosphate-*co*-carbonate) polymeric materials for Solid State Nuclear Track Detections (*manuscript under preparation).*

Patent filed:

1. V. S. Nadkarni and **D. G. Naik**, ***Indian Patent No. 201621021793***, entitled "Allyl Thiodiglycol Sulfone Carbonate, polymers thereof and their use in detection of ionizing radiations."

Papers presented/ attended at National/ International conferences:

1. **D. G. Naik** and V. S. Nadkarni, Polytriallyl phosphate (PTAP) and its copolymers for solid state nuclear track detection; *18th National symposium on SSNTD's and their applications*, organized by Aggarwal College Ballabgarh Faridabad, Haryana during October 18-20, 2013.
2. **D. G. Naik** and V. S. Nadkarni, Polymerization of Triallyl Phosphate (TAP) and mixture of (ADC-TAP) and Application in Solid State Nuclear Track Detection; *ACT NCCT-2014 National conference on "Emerging Area in Chemical Education & Research and National Convention on Chemistry Teachers"*, organized by The IIS University, Jaipur on 16-18 October 2014.
3. **D. G. Naik** and V. S. Nadkarni, Development of Novel poly (TAP-*co*-PETAC) and poly (TAP-*co*-NADAC) polymeric materials for solid state nuclear track detection studies; *National Symposium on "Materials Characterization and Manufacturing (MCM-2016)*", organized by P. C. College of Engineering, Verna, Goa in collaboration with Department of Physics, Goa University, Goa held on 18th and 19th August 2016.
4. **D. G. Naik**, V. S. Nadkarni, "Phosphorus containing polymeric materials for solid state nuclear track detection- A brief review" *in International conference and exhibition on Polymer Chemistry at Atlanta, USA accepted for E-poster presentation* held on 14th -16th November 2016.
5. **D. G. Naik**, V. S. Nadkarni, "Poly (sulfone-carbonate) Polymers for Swift Detection of Charged Particle Tracks: A Replacement for Commercially available PADC Nuclear Track Detectors", (Oral presentation) at *20th National conference on SSNTDs and their applications*, organized by VVIET, Mysuru on October 26-28, 2017.

6. Attended one day workshop entitled "IPR and National Innovation system in India" organized by NRDC New Delhi & co-organized by Goa university Goa on 13th December 2013.
7. Participated in the conference on "Chemical Industrial Disaster Management (CIDM): Chemical, Pharmaceutical & Hydrocarbon Industry" organized by Federation of Indian Chambers of Commerce and Industry at Cidade De Goa, Goa on 29th September – 1st October 2014.
8. Participated in the International Conference on Green Chemistry in Goa University, Goa on 22nd - 24th January 2015.
9. Participated in the National Conference at IXth J-NOST Conference for Research Scholars in IISER-Bhopal, Madhya Pradesh on 4th - 6th December 2013.