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First report on preparation of poly (nitro-carbonate) thermoset polymers for nuclear track detection

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ABSTRACT

In an attempt to study the effect of various radiation sensitive groups in the polymer matrix and their relation to the sensitivity towards charged particles, we have designed two new monomers Allyl bis-(2-nitroxy-ethyl) carbamate (ABNEC) and prepared its copolymer with ADC. Since, the ABNEC monomer was not thermally much stable, we designed another novel monomer containing ($-CNO_2$) group, called tris-(2,4-dioxa-3-oxohept-6-en-1-yl)nitromethane (TDONM) and prepared its homopolymer as well as copolymer with ADC. These are thermoset poly(nitro-carbonate) materials and are being reported as track detectors for the first time. The kinetics of polymerization for these monomers was studied. Due to thermal instability of ABNEC and TDONM monomers, special care is required during their polymerization. The preliminary studies carried out show that, the copolymers ABNEC-ADC and TDONM-ADC are almost comparable to PADC track detectors. A brief description of the study of some of the etching conditions, the effect of initiator concentration on the alpha sensitivity of the materials and also track detection efficiency studies in comparison with commercially available PADC (Pershore Moldings, UK) are reported.

1. Introduction

Since the advent of Solid state nuclear track detection (SSNTD) technique (Young, 1958) a number of polymers have been used to detect charged particles. The most commonly used plastic materials as nuclear track detectors are the cellulose nitrate (LR-115)™, poly allyl diglycol carbonate (PADC) (CR-39)™ and Bisphenol A polycarbonate (Lexan)™. Poly allyl diglycol carbonate (PADC) polycarbonate (Cartwright et al., 1978) replaced most of the plastics due to its very high sensitivity to many charged particles, and superior optical properties. The relation between sensitivity of a particular material to charged particles and its structural features has always remained a matter of interest for SSNTD workers, though a few attempts in this direction are known (Fujii and Yokota, 1988; Fujii et al., 1990).

We have been working on the preparation of plastic materials as SSNTDs, since 1996 (Nadkarni and Samant, 1996). We have reported our preliminary efforts towards casting of homo and copolymers films from novel monomers (Nadkarni et al., 2003a, b) *N*-allyloxycarbonyl diethanolamine-bis(allyl carbonate) NADAC monomer along with allyl diglycol carbonate (ADC) monomer. In continuation of our efforts to prepare more sensitive materials and to study the effect of various functional groups on the sensitivity of the films we synthesized two novel monomers. Since cellulose nitrate (LR-115)™ films containing the nitrate ester groups are found to have a good sensitivity towards alpha particles, the idea was to prepare thermoset materials by introducing nitrate ester ($-ONO_2$) and nitro groups ($-NO_2$) in the polymer (polycarbonate) matrix, and to study the effects of these groups on the sensitivity of the materials.

The first monomer, Allyl bis-(2-nitroxy-ethyl) carbamate (ABNEC) could not give its homopolymer and hence was copolymerized with ADC. This polymerization too, had some difficulties due to poor thermal stability of ABNEC under polymerization conditions (Nadkarni et al., 2004). As the thermal instability was considered due to ester ($-ONO_2$) groups (similar to thermal zinstability of nitrocellulose), we thought of synthesizing a new monomer containing ($-C-NO_2$) and compare its polymerization process and track detection characteristics with polymers derived from ABNEC. Tris-(2,4-dioxa-3-oxohept-6-en-1-yl)nitromethane (TDONM) was thus synthesized for this purpose.

In this paper, we present some preliminary results about the track detection properties of these novel homo and copolymers obtained from the aforesaid monomers. A brief description of the study of some of the etching conditions, the effect of initiator concentration on the sensitivity of the materials and also track

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detection efficiency studies in comparison with commercially available PADC (Pershore Moldings, UK) are reported.

2. Materials and methods

Indigenously prepared ABNEC and TDONM monomers, iso propyl peroxydicarbonate (IPP) initiator were used for the preparation of homopolymer called poly-[tris-(2, 4-dioxa-3-oxohept-6-en-1-yl) nitromethane] i.e. PTDONM and copolymers of, ABNEC-ADC and TDONM-ADC. PADC films from Pershore Molding (UK) of thickness 250 μm and our indigenously prepared NADAC-ADC copolymer of thickness 500 μm were used for comparative studies. Dioctyl Phthalate (DOP) plasticizer manufactured by S D Fine Chemicals, India was used as such. Glass plates (Schott, Germany), thin Teflon™ sheets, aluminium plates were used for assembling the polymerization moulds. The various steps involved in the synthesis and polymerization of the monomers are briefly described below. IPP was prepared in our laboratory and polymerization was carried out using a polymerization bath controlled using microprocessor based electronic temperature controller F25 HP, from Julabo, Germany.

2.1. Synthesis of monomers

2.1.1. Synthesis of ABNEC monomer

The monomer was synthesized in a two step process. Diethanolamine was treated with allyl chloroformate wherein Allyl bis-(2-hydroxyethyl) carbamate was obtained which was followed by its nitration to give ABNEC monomer in 80% yield. The reaction was carried out at low temperature 0–5 °C and time duration of 0.5–2 h. The reactions are illustrated in Scheme 1.

2.1.2. Synthesis of TDONM monomer

This monomer was synthesized by a two step process. Tris hydroxy methyl nitromethane was first prepared by formylation of nitromethane and was then treated with allyl chloroformate to yield TDONM (Scheme 2).

2.2. Preparation of mold

A square shaped gasket of Teflon of outer length 100 mm, with an inner window of length 80 mm, and thickness of 500 ± 10 μm was specially prepared for this purpose (Nadkarni et al., 2003a). It was sandwiched between two clean Schott brand optical glass plates of size 100 mm (l) × 100 mm (b).

2.3. Preparation of SSNTD films by cast polymerization

ABNEC and TDONM monomers were filtered carefully to remove any solid impurities. The monomers were stirred under nitrogen atmosphere to remove any dissolved air and oxygen, which hinder the process of polymerization. The mixture containing the monomer, initiator and plasticizer was carefully injected into the mold using a syringe, through a previously prepared tiny hole in the Teflon gasket. Special care was taken to avoid any air bubbles in the liquid monomer film during the injection in the mold. The mold was then sandwiched between two flat aluminium plates of uniform thickness and pressurized using wing-nut bolts fitted at the four corners of aluminium plates. The entire assembly was then kept in the polymerization bath and heated as per predetermined temperature–time intervals which in turn, obtained after a careful polymerization kinetics study of TDONM and ABNEC monomer/mixture of monomers. The polymerization temperature–time profile used for the polymerization is shown in Figs. 1. The mold was then allowed to cool slowly for another 12 h and then opened. A clear transparent and yellowish film of 500 ± 10 μm was obtained in this way.

2.4. Studies of etching conditions

Small pieces of size 10×10 mm^2 of homo and copolymer films prepared using 3.0% IPP initiator were used in the etching study. They were suspended vertically in an etching bath containing aqueous NaOH and the temperature was maintained using a constant temperature circulating water bath. The etching studies were carried out using varying concentration of NaOH and at three different sets of temperature.

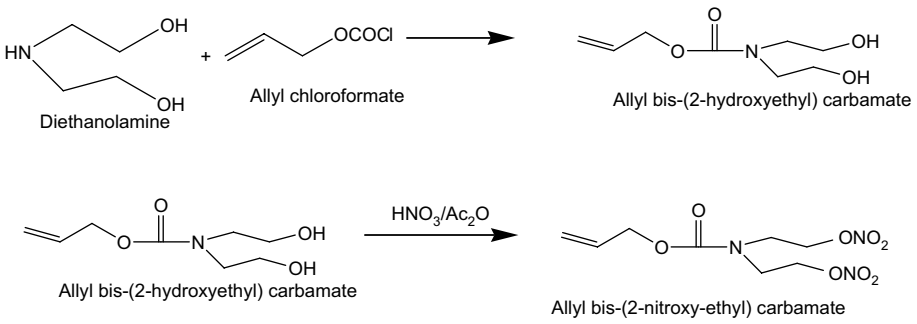
2.5. Determination of sensitivity of the films

The sample pieces of the homo and copolymer films were exposed to normally incident alpha particles and fission fragments from a ^{252}Cf in vacuum ($\sim$0.1 Torr) at a distance of 50 mm from the source and etched in 6 N and 4 N NaOH at 60 and 70 °C. The etch pit diameters were determined using an optical microscope (Carl Zeiss) at magnification of 40×. For the thickness measurement alpha meter (Para Electronics) with a least count of 1 μm was used. All the weight measurements were carried out using a digital single pan balance (Sartorius) having least count of 10^{-4} g.

3. Results and discussion

3.1. Preparation of the polymer

We have previously demonstrated that the kinetic model for polymerization of ADC monomer could be extended to other allylic monomers (Nadkarni et al., 2003a, b). We thus applied the same concept to our newly synthesized monomers. Thus, kinetic study was undertaken to find a suitable heating profile for the polymerization. It was found that polymer becomes colored if the heating is continued beyond 65 °C for both ABNEC as well as TDONM. Hence, a heating profile as shown in Fig. 1 above was chosen for the polymerization. Thus, thermal instability appears to be



Scheme 1. Synthesis of ABNEC monomer.