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Stannic chloride-*para* toluene sulfonic acid as a novel catalyst-co-catalyst system for the designing of hydroxyl terminated polyepichlorohydrin polymer: Synthesis and characterization



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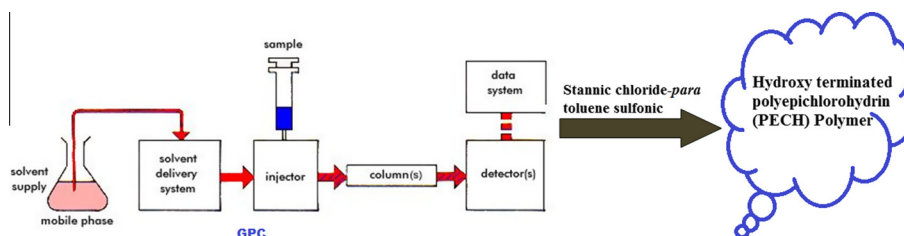
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HIGHLIGHTS

- Liquid hydroxyl terminated polyepichlorohydrin.
- A new catalyst co-catalyst combination of aromatic acid and Lewes acid.
- A bi-functional PECH, suitable for polyurethane as polyol.
- Effects of different molar ratios of catalyst co-catalyst on product quality.
- Effects of various parameters on product yield and product quality.

GRAPHICAL ABSTRACT

Stannic chloride-*para* toluene sulfonic acid was used as a novel catalyst-co-catalyst system for the preparation of PECH. Molecular weight distribution and polydispersity of the polymers were determined by Gel permeation chromatography (GPC).



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ABSTRACT

Hydroxy terminated polyepichlorohydrin (PECH) was synthesized in good yield (85–88%) with improved functionality (2.01–2.53) and desired number average molecular weight (~3000), using a novel catalyst-co-catalyst combination. The effect of various molar ratios (4–12) of *p*-toluenesulfonic acid and SnCl₄ on molecular weight of PECH was investigated. Different polymerization conditions like temperature, time and monomer addition rates were found to have pronounced effect on molecular weight, polydispersity and functionality of the products. The molecular weight distribution and polydispersity of the synthesized polymers were determined by Gel permeation chromatography (GPC). Absolute value of Number average molecular weight (M_n) was established with vapor pressure osmometry and structural elucidations were carried out by FT-IR and NMR spectroscopic techniques. Terminal Hydroxyl groups were quantified by acetylation method and functionality was derived from hydroxyl value and M_n.

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1. Introduction

During last few decades multiple efforts have been made to improve the performance of solid rocket propellants, capable to

satisfy the insensitive munitions requirements and complying with current international environmental regulations with reduced cost. The use of energetic binder is considered to be one of the practical ways to improve the energy and other technical performances like thrust and specific impulse of solid rocket propellants. Azido polymers have attracted researcher's attention, since azido group contributes 685 kJ mol⁻¹ energy due to exothermic session of azide group [1]. Among different azido polymers, glycidyl azide polymer (GAP) has been emerged as a strong candidate for future aerospace

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applications as energetic binder [2]. GAP is cured with di or tri isocyanate to give polyurethane network structures for composite propellants. GAP is produced by nucleophilic substitution of chloro group with azide group in polyepichlorohydrin (PECH). So PECH is utilized as a basic starting material for the preparation of GAP [3].

PECH is produced by polymerization of epichlorohydrin (ECH), having halide and epoxide as functional groups. Epoxides have high degree of strain in the three member ring and generally be polymerized, by both cationic and anionic polymerization [4,5]. As ECH has chloromethyl group, which has pronounced probability to react with nucleophile, therefore anionic polymerization of ECH is restricted. So, cationic ring opening polymerization of epichlorohydrin (ECH) is a preferred choice for the synthesis of PECH.

The strong basicity of the oxygen atoms makes the three membered ring of oxiranes very likely to be opened *via* cationic mechanism. A variety of initiator systems can be utilized to generate the secondary or tertiary oxonium ion propagation species (Fig. 1) [6]. The α -carbon of the oxonium ion, being electron deficient because of the adjacent positively charged oxygen, is attacked by the oxygen atom of ECH monomer molecule. Polymerization of ECH in the presence of Lewis acids like SnCl_4 , BF_3 , SbCl_5 or FeCl_3 [7] is reported earlier. Different protic compounds such as water, alcohols or diols, trichloroacetic acid and trifluoroacetic acid are the most commonly used co-catalysts [8,9].

The ring opening polymerization of ECH in the presence of a diol and Lewis acid (SnCl_4 and BF_3) takes place either by activated chain end (ACE) or activated monomer (AM) mechanism [10]. The dominance of both mechanisms depends upon the relative diol catalyst ratio. If 1 or 2 mol of diol are used per mole of BF_3 etherate or SnCl_4 then only ACE mechanism operates while if more moles of diol are used per moles of catalysts then ACE as well as AM mechanisms operates [11]. The relative proportion of these two mechanisms also depends on different polymerization conditions. Higher temperature and slow addition of ECH favors the AM mechanism resulting in linear polymer with high molecular weight thus reducing polydispersity, whereas the low temperature and the faster addition of ECH favors ACE mechanism giving predominantly oligomers and cyclic products with reduced Mn and increased polydispersity. Yu [12] tried to isolate these oligomers/cyclic compounds which do not have hydroxyl functionality and hinder proper curing with diisocyanates [8,11,13,14]. The ideal hydroxyl functionality of GAP is two for its subsequent curing whereas the required Mn for achieving optimum mechanical properties of solid rocket propellant ranges from 1500 to 5000 [14–19]. Molecular weight and hydroxyl functionality of GAP are important parameters which depict the mechanical properties of the final propellant, which on the other hand depends upon the nature of PECH.

The main objective of the present work is to develop a method for the production of bi-functional PECH capable to produce binder grade GAP (Molecular weight 1500–5000). In this study we have used the *p*-toluene sulfonic acid (*p*-TSA) as co-initiator with stannic chloride (catalyst). The effects of catalyst co-catalyst ratios on molecular weight, hydroxyl value, polydispersity and yield of the PECH were explored in the present work. *p*-TSA was used for the

first time as co-catalyst along with stannic chloride, therefore, it was necessary to study its effects on the product quality which was investigated in terms of different polymerization conditions like temperature, time, inert atmosphere and addition rate of ECH. Water (as moisture content of ingredients) has found to have pronounced effect on the product quality, therefore effect of total moisture (in reagents like *p*-TSA, SnCl_4 and ECH) on Mn, polydispersity and cyclic product formation was also explored.

2. Experimental

2.1. Materials

Epichlorohydrin (commercial grade) was refluxed with CaO distilled and fraction collected at 110–115 °C was stored on molecular sieves (0.05% moisture). SnCl_4 , chloroform and ethanol were used as received. *p*-TSA monohydrated ($\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$) was dried under reduced pressure at 60 °C for 2 and 4 h to attain 9% and 3% moisture, respectively and stored in desiccators over silica gel.

2.2. Analytical techniques

The functional group characterization of the product was done by using FT-IR spectrophotometer (Nicolet 50) with ATR assembly. A Gel permeation chromatograph (GPC) instrument connected with HPLC Pump (515 of Waters Associates), refractive index detector (Shimadzu RID-6A) and three styragel columns (100, 500 and 1000 Å) were used in descending order. Tetrahydrofuran (THF) was used as a mobile phase with 1 mL/min flow rate. Samples were prepared in THF with a concentration of 0.12% w/v. The molecular weight distribution and polydispersity of the samples were determined by calibrating the instrument with polystyrene standards of 500, 1300, 5000, 10,500 and 130,000 Da. Absolute molecular weight of polymer was determined by vapor pressure osmometer (VPO, Kneur K 7000 Germany) in chloroform at 43 °C. The instrument constant (*K*) was determined by benzil (AR grade) and calibration of the instrument was verified by polystyrene standard.

^1H and ^{13}C spectra of the samples were recorded by Bruker Avance 300 spectrophotometer operating at 300 MHz for ^1H and at 75 MHz for ^{13}C , using deuterated-chloroform as solvent and tetramethyl silane (TMS) as internal reference.

Hydroxyl functionality of the final product was derived from Mn (by VPO) and hydroxyl value by using the below given equation. Later was determined by reacting acetic anhydride with terminal hydroxyl groups of PECH as per ASTM standard D-3446.

$$\text{Functionality } (f) = \frac{\text{Mn} \times \text{hydroxyl value (mmol of KOH/g)}}{1000}$$

Oligomers/cyclic products were extracted from polymer by ethanol and quantified gravimetrically. The % yield was calculated by using the general equation:

$$\% \text{ Yield} = \frac{\text{Actual yield (g)}}{\text{Theoretical yield (g)}} \times 100$$

2.3. Polymerization

All the reactions were conducted in a reactor equipped with a mechanical stirrer, temperature and atmosphere (N_2 or Air) controller. Stoichiometric amounts of ECH were added drop wise to *p*-TSA with continuous stirring at 60 °C. After 20 min the mixture was cooled to room temperature, predetermined amount of SnCl_4 was added to it and the mixture was stirred for further 10 min.

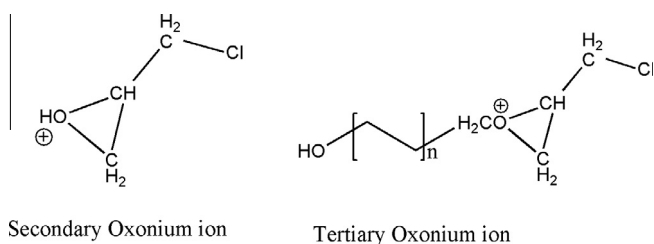


Fig. 1. Structure of secondary and tertiary oxonium ions.

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