SYNOPSIS

The thesis entitled **"Conducting polyurethanes and polyureas with oligoanilines: Synthesis, characterization and their electrochemical applications"** has been divided into six chapters.

CHAPTER-I	**:**	Introduction of polyurethanes, conducting polyaniline and conducting oligoanilines: application prospects
CHAPTER-II	**:**	Conducting polyurethanes with trianilines and tetraaniline
CHAPTER-III	**:**	Moisture curable polyurethanes with tetraaniline
CHAPTER-IVA	**:**	Electro active hybrid polyurethane with tetraaniline pendant groups
CHAPTER-IVB	**:**	Investigations on anticorrosive, thermal and mechanical properties of conducting polyurethanes with pendent tetraaniline groups
CHAPTER-V	**:**	Aniline-nonamer segmented polyurea-electrochemical sensing and corrosion evaluation
CHAPTER-VI	**:**	Summary and conclusions

CHAPTER I: Introduction

New hybrid conducting polyurethanes:

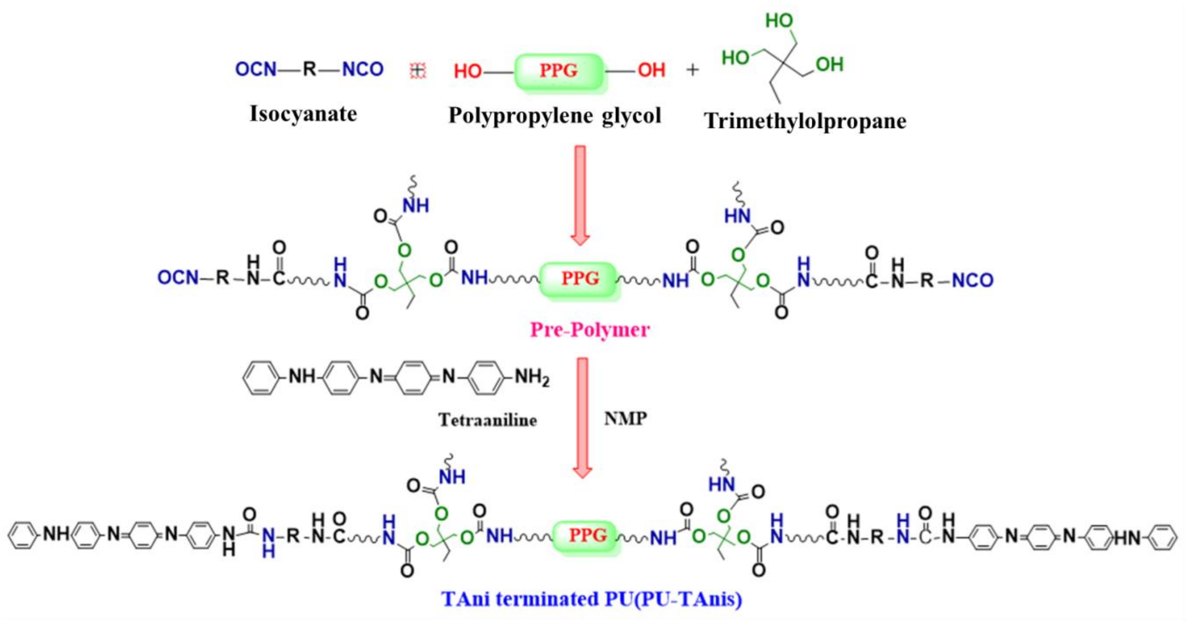
The conventionally known polymers, such as polyethylene, polyesters, epoxy polymers, polyurethane and PVC are highly processable with good mechanical and thermal properties. However these are electrical insulators barring them for applications in electrical conducting devices. There have been many attempts in literature to bring electrical conductivity to these insulating polymers, so that the application prospects of these robust polymers are widened.

Binary composite systems, comprising of conductive fillers such as carbon black (CB), carbon nanotubes (CNTs), or metal powder in the polymer matrix, resulted in materials that are tough, flexible, and electrically conductive. These distinctive materials are suited for mainly antistatic layers, electromagnetic interference shielding (EMI) chemical vapour sensors, and thermal resistors. Three main important applications of electrical conducting plastics are (a) antistatic, (b) electrostatic dissipation (ESD), and (c) electromagnetic interference shielding (EMI). Antistatic applications involve materials that exhibit surface resistivity of 10^{12}–10^{6} ohm cm and ESD applications involve imparting sufficient conductivity to plastics to reduce their surface resistivity to the range 10^{6}–10^{4} ohm cm. Usually conductive polymeric materials offer conductivity in the range 10^{-3}–10^{-6} S cm^{-1}, which is also optimum conductivity sufficient for the electromagnetic interference shielding (EMI) and ESD applications. The conductive polymer composites/blends are useful materials for sensors, electrostatic dissipaters, EMI shielding components, shape memory and corrosion protection coatings. The chapter-I gives insights into literature of polyurethanes and conducting polymers and gives rationale for taking this work which formed basis of thesis.

An attempt has been made to understand the structure-property relationship through the extensive characterization of synthesized molecules such as oligomers (oligoanilines) and conducting polyurethane materials. The spectroscopic techniques such as Fourier transform infrared spectroscopy (FT-IR), ^{1}H nuclear magnetic resonance spectroscopy (NMR), UV-Vis spectroscopy, mass spectrometry techniques such Matrix-assisted laser desorption/ionization (MALDI), X-ray diffraction (XRD) etc. have been used to obtain the structural information wherever required. The surface of the samples was analyzed by using X-ray photoelectron spectrometer (XPS) at room temperature. Similarly, the microscopic techniques such as optical microscopy (OM), field emission scanning electron microscope (FE-SEM), transmission electron microscopy (TEM) and atomic force microscope (AFM) have been used for morphological evaluation wherever required. The techniques such as the thermo gravimetric analysis (TGA) for degradation profile, universal testing machine (UTM) for tensile properties and differential light scattering (DSC) for determination of glass transition temperature have been used in this study. The mechanical properties have been studied by DMTA experiments on the films. Conductivity of the powder/films of conducting polymers is measured by four probe method using. The electrochemical studies (such as cyclic voltammetry (CV)) for sensing behaviour were performed using in a three-electrode electrochemical cell using SCE as the reference electrode and platinum wire as the counter electrode. The anti-corrosive studies of the coating films have been carried out on selective coating films as per the requirement. Thus an attempt has been made to understand the structure property relationship through the extensive characterization of synthesized molecules, oligomers and hybrid conducting materials developed in this study.

CHAPTER II: Conducting polyurethanes with trianilines and tetraaniline

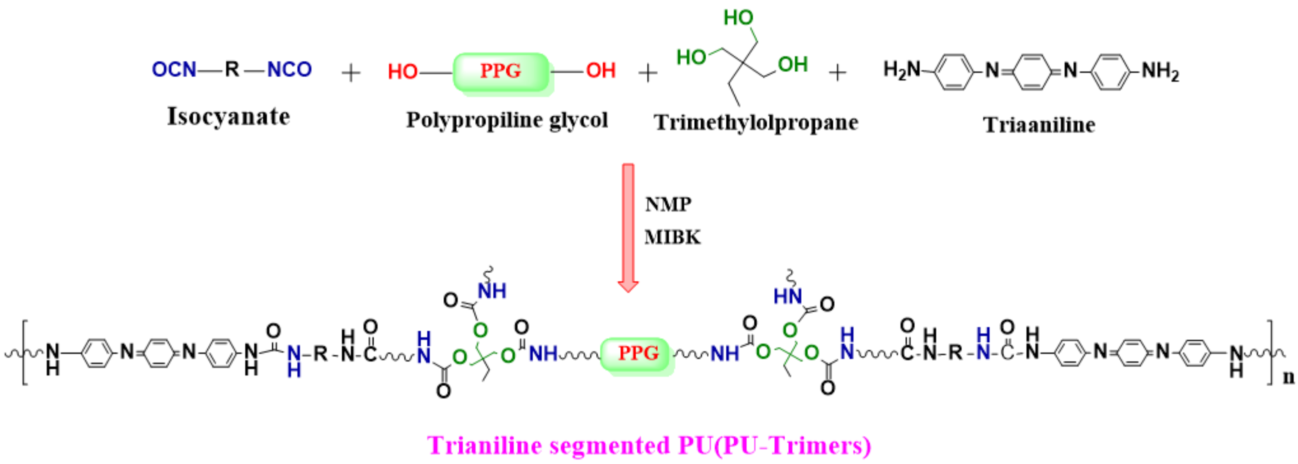
This chapter reports a novel conducting polyurethanes (CPUs) containing oligoanilines, namely tetraaniline (TAni) (PU-1 to PU-6) or trianiline (TriAni) (PU-7 to PU-12), in the backbone of polyurethane and these have been synthesized and characterized by formal spectral techniques. The unique properties of these CPUs, viz., electronic conductivity and electrochemical activity arising from the presence of oligoaniline units have been evaluated. The basic polyurethane backbone is derived from toluene diisocyanate (TDI), Isophorone diisocyanate (IPDI) or hexamethylene diisocyanate (HMDI), and polypropylene glycols of molecular weight 425 and 2000. In the first category of polyurethanes, the prepolymer obtained from the above reactants were chain terminated by TAni in emeraldine base. The conductivity of these CPUs films ranged from 1.2×10^{-5} to 1.77×10^{-3} S/cm. These polymers showed lower conductivity due to the presence of nonconjugated polyurethane segments. The second category of CPUs is obtained from prepolymers by chain extension with TriAni. The conductivity of these polymers is similar to the TAni analogues but are electrochemically inactive. The anticorrosion properties of two of these polymers have also been evaluated in this study. The syntheses of CPUs are shown in Scheme-2.1 and Scheme-2.2.



PU Synthesised	Isocyanate	Polyol
PU-1	TDI	PPG-425
PU-2	TDI	PPG-2000
PU-3	IPDI	PPG-425
PU-4	IPDI	PPG-2000
PU-5	HMDI	PPG-425
PU-6	HMDI	PPG-2000

Scheme-2.1 Synthesis of Tetraaniline containing conducting polyurethanes

All the conducting polyurethanes obtained by Scheme-2.1 and Scheme-2.2 were characterized by various spectroscopic techniques. Amine capped tetraaniline and trianiline oligomeric units in emeraldine base (EB) oxidation state have been used as chain terminator/ or extendor. The PU-TAnis exhibited irreversible two electron transfers whereas the PU-trianilines did not show electrochemical activity. The conductivity of the films of these new polymers is lower to their oligomeric anlaogues. The corrosion protecting ability is more for tetraniline containing polyurethane compared to trianiline containing polyurethane.



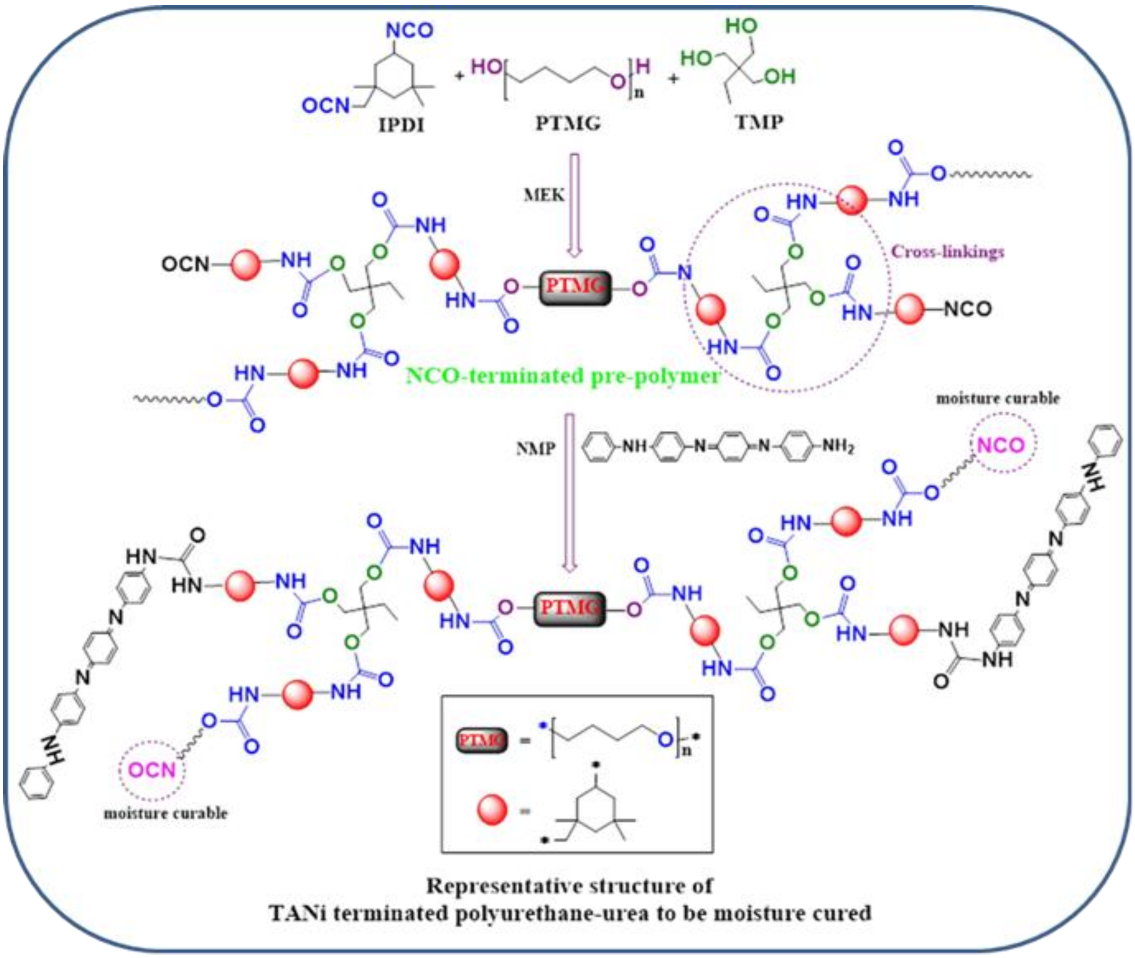
PU Synthesised	Isocyanate	Polyol
PU-7	TDI	PPG-425
PU-8	TDI	PPG-2000
PU-9	IPDI	PPG-425
PU-10	IPDI	PPG-2000
PU-11	HMDI	PPG-425
PU-12	HMDI	PPG-2000

Scheme-2.2 Synthesis of Trianiline containing conducting polyurethanes

CHAPTER III: Moisture curable polyurethanes with tetraaniline

In general moisture-curable polyurethanes are widely known for protective and decorative coatings in a broad range of application because of their wide range of physical properties. The work described in the previous chapter, it was observed that the film formation was very slow and the films were brittle. The corrosion protection was moderate, not high as expected. The electrochemical properties were not uniform. Hence polymers with better improved properties are designed and synthesised in this chapter-III.

This chapter reports preparation of new series of electrochemically active conducting polyurethanes (CPU) using tetraaniline as conducting unit with IPDI-PTMG as urethane prepolymer segment. These films are robust and formed as a consequence of moisture curing of excess isocyanate. The films are novel in the sense that the conductivity is found to be in the higher side of the order of 10^{-3} S/cm and the tetraaniline segments are electrochemically oxidiazable and/or reducible. The formed films have been subjected for thermal and mechanical tests such as TGA, DSC, DMTA and tensile tests to explore into the understanding of structure–property relations. The nano/microstructure of the polymers has been investigated by TEM analysis. These CPUs are found to be excellent anti-corrosion barrier coatings for mild steel. The synthesis has been carried out using Scheme-3. The results are presented and discussed in this chapter-III.

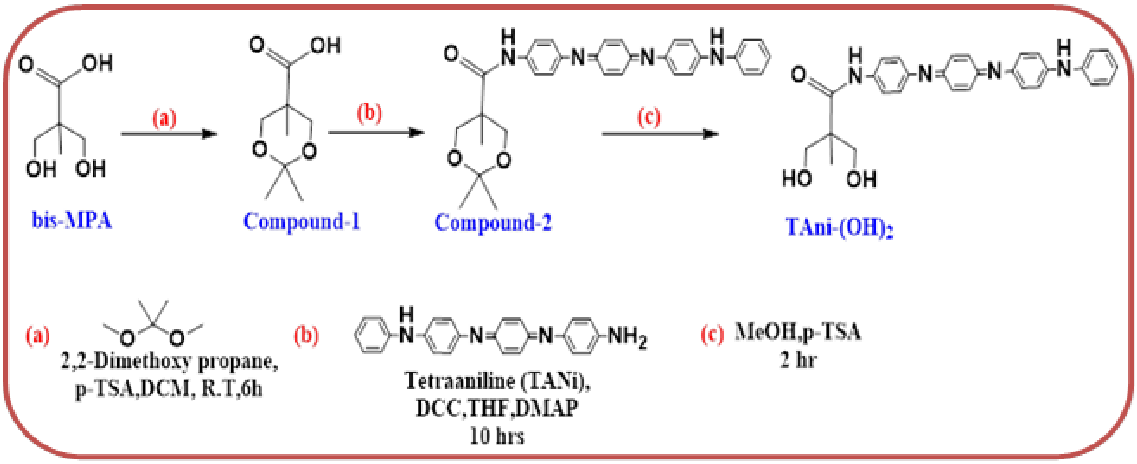


Scheme-3.1: synthesis of tetraaniline containing moistre curable conducting polyurethane

CHAPTER IV(A): Electro active hybrid polyurethane with tetraaniline pendant groups

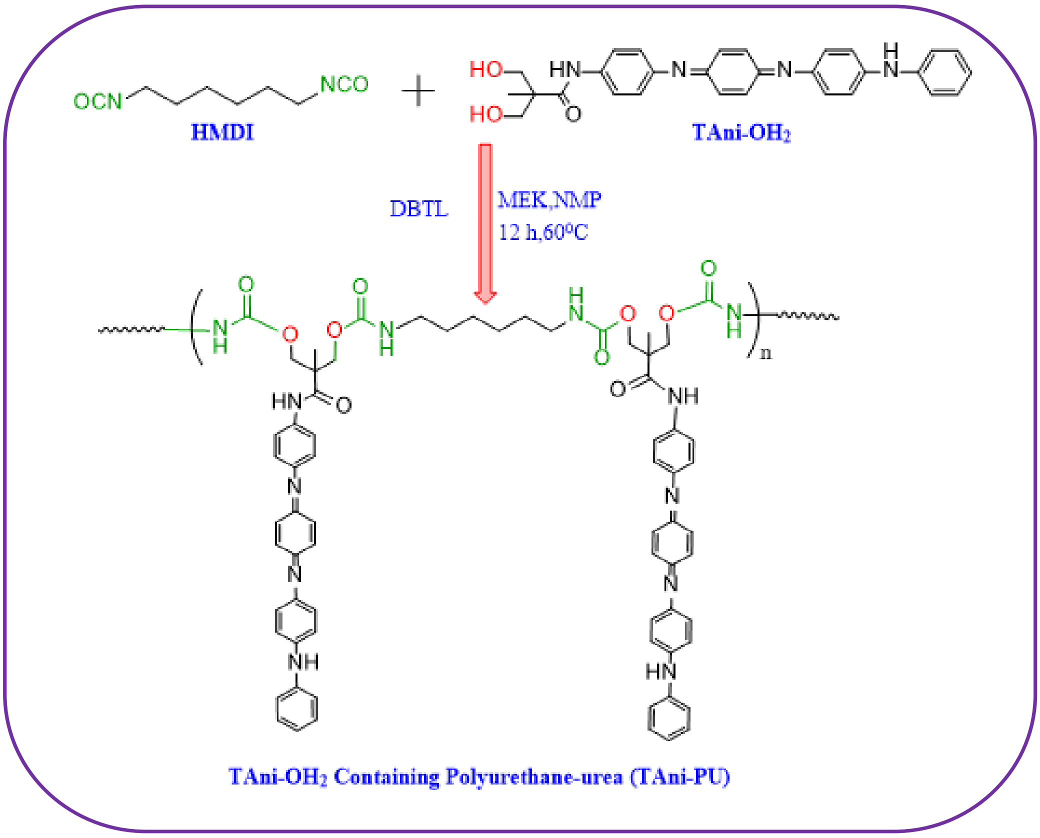
To further enlarge applications of conducting polyurethanes, there have been attempts to bring conductivity and electrochemical activity to this insulating polymer. There is no report available in literature in which tetraaniline is bonded via a –O-C(=O)-NH- (urethane) bond to give polyurethane.

Chapter-III describes, synthesis of a novel hybrid polyurethane from tetraaniline-diol (TAni-$(OH)_2$) and hexamethylene diisocyanate (HMDI) with pendant tetraaniline units on the back bone. The synthetic procedure shown in Scheme-4A.1 and Scheme-4A.2. The striking property of this unprecedented polyurethane is its electrochemical sensing of ascorbic acid and self-assembly into core-shell type microstructures (microcapsules) in presence of aqueous acetic acid/noctane interface. These microcapsules exhibited a wide range of pH responses in their absorption spectrum. The synthesized polyurethane containing pendant tetraaniline units showed good surface conductivity to the tune of 3.4×10^{-4} S/cm. The electrochemical investigation showed two single electron oxidations and two single electron reductions reversibly.



Scheme 4A.1 Chemical Synthesis of TAni-$(OH)_2$

We also investigated electrochemical sensing details of carbon paste electrode (CPE) fabricated with conducting polyurethane (TANI-PU) as ascorbic acid sensor (vitamin C, AA) in 0.2 M and pH 7 phosphate buffer solution. The fabricated electrode is useful in sensing as low as 1 mM of ascorbic acid. Self-assembly property was probed by optical and TEM studies which established the core-shell structure of the assembled species. The self-assembled microcapsules exhibited pH dependent doping and dedoping processes as established by UV-Visible study. The results are presented and discussed in thesis chapter-IV(A).

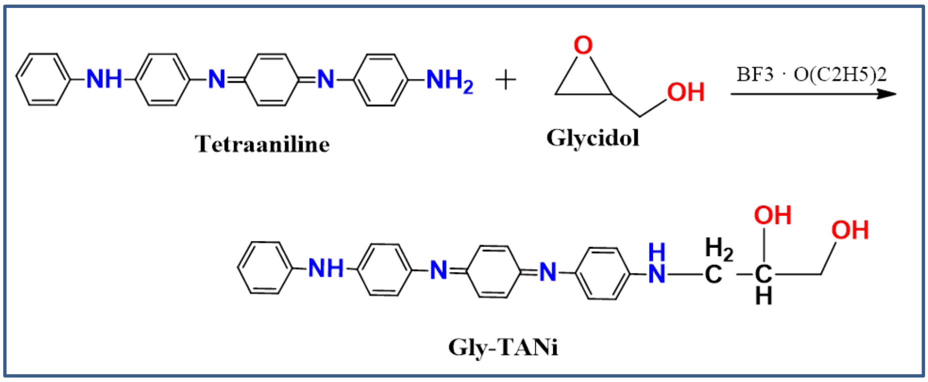


Scheme 4A.2 Chemical Synthesis of TAni-PU

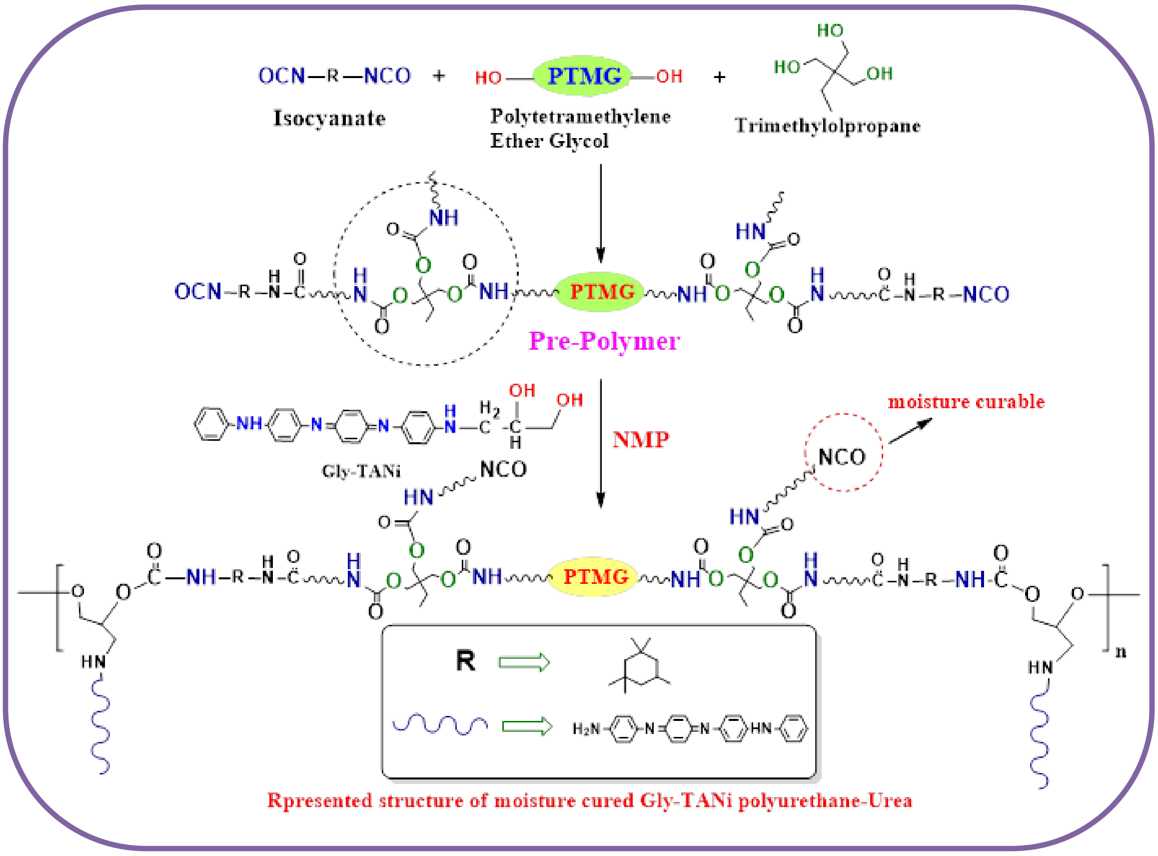
CHAPTER-IV(B): Investigations on anticorrosive, thermal and mechanical properties of conducting polyurethanes with pendent tetraaniline groups

This part of the chapter reports synthesis of novel conducting polyurethanes synthesized from tetraaniline-diol namely Gly-TAni. In the earlier chapter-IV(A) we successfully functionalised the TAni with bis-MPA (2,2-bis(methoxyl) propionic acid in two step process namely Bis-TAni and in this part another new diol Gly-TAni is synthesised in easy process by using tetraaniline(TAni) and glycidol through SN^2 reaction in single step process. The reparations of Gly-TAni containing conducting polyurethanes (GCPU-5%, GCPU-10%, GCPU-12.5% and GCPU-15%) were carried out in two step reaction sequence. The synthetic procedure shown in Scheme-4B.1 and Scheme-4B.2. The synthesized polyurethane containing pendant tetraaniline units (both Gly-PU) showed good surface conductivity to the tune of 5.41×10^{-3} to 3.69×10^{-4} S/cm. The electrochemical investigation showed two single electron oxidations and two single electron reductions reversibly. The anticorrosion properties of these polymers have also been evaluated in this study and better corrosion resistance performed by

GCPU-15% which is assigned to 1.84 x 10^{-3} mm/yr. The films have been subjected for thermal and mechanical tests such as TGA, DSC, DMTA and tensile tests to explore into the understanding of structure–property relations.



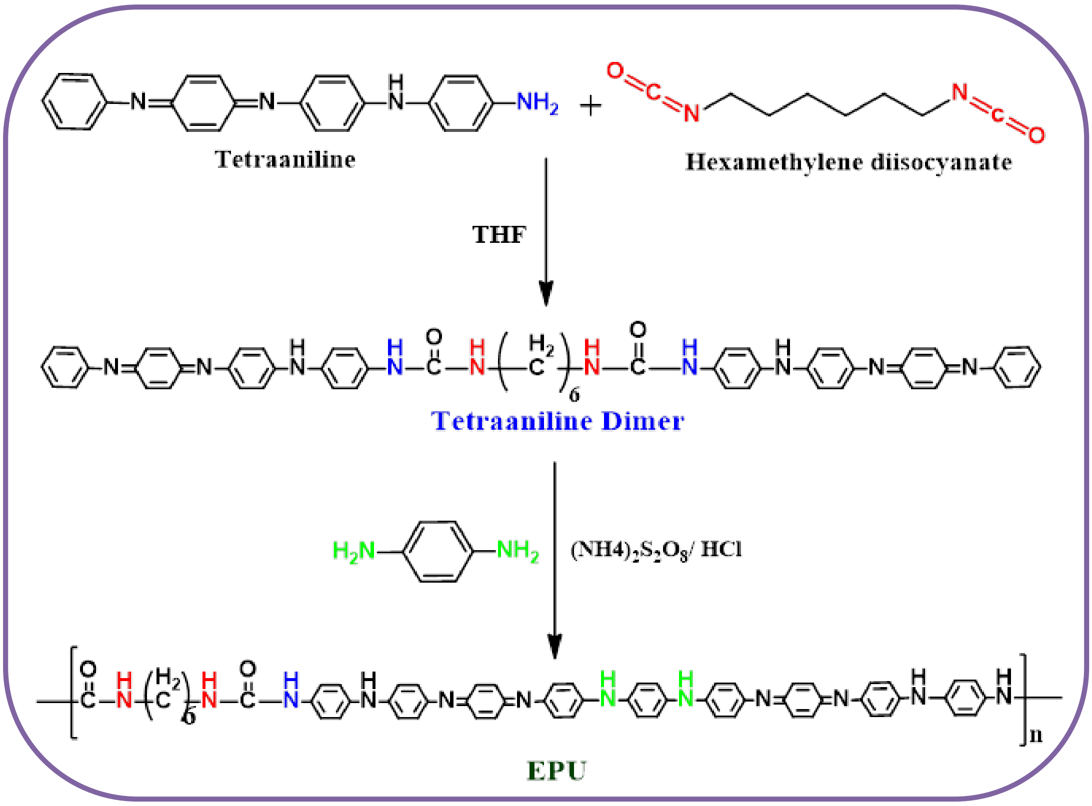
Scheme-4B.1 Synthesis of Gly-TAni



Scheme 4B.1 Chemical Synthesis of conducting polyurethanes of Gly-TAni

CHAPTER V: Aniline-nonamer segmented polyurea-electrochemical sensing and corrosion evaluation

The previous Chapter-III and Chapter-IV(A) described couple of electroactive polymers bearing oligoaniline (tetraaniline) segments, which exhibited high corrosion resistance on mild steel (MS) and excellent electrochemical sensing for ascorbic acid and self-assembly into core shell type microstructures (microcapsules) in presence of aqueous acetic acid/n-octane interface. In this chapter, we synthesized an A-B-A type block copolymer polyurea with Tetraaniline dimer (TD) with 1, 4-Phenylenediamine by oxidative coupling, resulting in aniline nonamer in the main chain. The corrosive protection of EPU for MS, as the main part, was investigated and results are presented and discussed below in detail.



Scheme 5 Chemical Synthesis of Electroactive polyurea

CHAPTER-VI: Summary and conclusions

This chapter summarizes the important findings of this work and also explains the scope of the future perspectives.