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Synthetic investigation of glycine catalyzed triarylimidazole based organophosphorous heterocyclic functionalized vinyl polymer – A green approach

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ABSTRACT

In the present investigation, an efficient and environmentally adopted synthesis of triaryl substituted imidazole in one-pot was reported. The multicomponent reaction between various aldehydes, benzil, benzoin, ammonium acetate and glycine under solvent free condition has been explained. Instead of using toxic reagents for the synthesis of heterocyclic compounds, Glycine has been selected as a green catalyst due to simple work-up procedure, shorter reaction time and high yield. The synthesized imidazole derivatives on further treatment with phosphorous oxychloride resulted in an organophosphorous containing N-heterocyclic compound (N-P) thus by altering acidic hydrogen of imidazole. Further, N-P was reacted with polyvinyl alcohol resulted into organophosphorous N-heterocyclic vinyl polymers. The synthesized vinyl polymers were characterized using, FTIR, NMR and Mass spectral studies. Results of the spectral studies were well supported the formation of the compounds. Thermal stability have also been studied using TGA.

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1. Introduction

To design and conduct chemical reactions with "green" experimental protocol is an enormous challenge that chemists have to confront to improve the quality of the environment for present and future generations. Target areas for achieving such a goal are the exploration of alternative reaction conditions and reaction media to accomplish the desired chemical transformations with minimized by-products or waste, over the past several years, chemists have been aware of the environmental implications of their chemistry. Nowadays, they are trying to develop new synthetic methods, reaction conditions, and uses of chemicals that reduce risks to humans and the environment. The compounds with an imidazole ring system have many pharmacological properties and play important role in biochemical processes (Lambardino and Wiseman, 1974). Many of the substituted imidazoles are known as inhibitors of fungicides and herbicides, plant growth regulators and therapeutic agents (Welton, 1999). Recent advances in green chemistry and organometallic chemistry have extended the boundary of imidazoles to the synthesis and application of a large class of imidazoles as ionic liquids and imidazole related N-heterocyclic carbenes (Lantos et al.,1993). There are several methods have been reported in the literature for the synthesis of imidazoles such as hetero-Cope rearrangement (Wolkenberg et al., 2004). Four-component condensation of aryl glyoxals, primary amines, carboxylic acids and isocyanides on Wang resin, reaction of N-(2-oxo)-amides with ammoniumtrifluoroacetate, 1,2-amino alcohols in the presence of PCl_5, diketones, aldehyde, amine and ammonium (Sharma et al., 2006). Several microwave (MW) assisted syntheses of imidazoles from 1, 2-diketones and aldehydes in the presence of a variety of catalysts such as silica-gel, silica-gel/HY,Al_2O_3, DMF, acetic acid (Heravi et al., 2007). $ZrCl_2$ (Siddiqui et al., 2005). $NiCl_2.2H_2O$ (Mazaahir Kidwai, et al., 2007) and ionic liquid (Moritani and Kajitani, 1997) also by using thiourea (Sakurada, 1958). In view of the inherent properties of glycine viz., environmental compatibility, non-corrosive, ready availability and cost effectiveness; this catalyst has started evoking interest in the organic synthesis (Maruhashi, 1992a,b). Phosphorus-containing compounds showed their usefulness in the preparation of water-soluble polymers (Maruhashi, 1992a,b; Petreus et al., 2005). Incorporation of Phosphorous unit into PVA showed improved flame retardancy, thermal oxidative stability, and good adhesion (Hamciuc et al., 2007). Phosphorus-containing polymers meet the requirements of low toxicity and low smoke during combustion for environmental and health considerations (Wang et al., 2002, 1998). The synthesis of polymers that contains

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phosphorus in the main chain or side chain attracts the interest of polymer specialists (Karpagam and Guhanathan, 2013; Chang and Chang, 1999). Phosphorus-containing polymers are able to increase the char during burning and thus decrease theamount of flammable zone and reduce the heat transfer from the flame to the material (Nishino et al., 2002; Chiang and MA, 2002). Poly(vinyl alcohol) (PVA) is a nontoxic, water-soluble, biocompatible, and biodegradable polymer, which is widely used in various applications such as fibers for clothes, industries, films, and membranes, materials for drug-delivery system, and cancer cell killing embolic materials. PVA fibers, gels, and films are potentially high performance materials because they have high tensile strength and modulus, excellent impact strength, high abrasion resistance, excellentalkali resistance, and oxygen barrier propertyare superior to those of any known polymer. Functional modification of PVA or introducingfunctional groups into the polymer chain has been believed to have basic significance with expanding its application. Many research articles have been reported concerning with the modification of polymer for the purpose of introducing carboxylic, sulfonate, and amino groups.The synthesis of PVA that containsphosphorus and heteroaromatics in the mainchain attracts the attentions of many researchers due to their peculiar characteristics viz, non-flammability, thermal stability, high melting points, and appreciable biological activities. Among the nitrogen-containing compounds, six-membered heterocyclic compounds are used in various applications as herbicides,insecticides, pharmaceuticals, and adhesives. Five membered heterocyclic compounds are used in electrical and pharmaceutical applications (Karpagam et al., 2008; Liu and Chiu, 2003). While analyzing the literature, considerable attention has been paid for phosphorus-containing polymers perhaps there was not much report on biologically active phosphorus-containing polymers. Hence, the scope of the present investigation was devoted to synthesize of phosphorus-containing nitrogen heterocyclic-based polymer by the reaction of PVA with nitrogen heterocyclicphosphonyl dichloride. The properties of the modified polymers such as thermal (TGA),Spectral (FTIR, and NMR), and biological activities have also been investigated and compared.

2. Experimental section

2.1. Materials and methods

The ultra pure chemicals viz., benzil, 4-chlorobenzaldehyde, ammonium acetate**,** glycine, dimethylformamide, phosphorous oxychloride, tetrahydrofuran and triethylamine were purchased from Merck, Mumbai and PVA (MW = 14,000) with a degree of hydrolysis of 98–99% were used as such. Silica gel (TLC and Column grade) was purchased from Merck. ^{1}H&^{13}C NMR (400 MHz) spectra were recorded on a Bruker Advance III 400 MHz multi nuclei solution NMR. FTIR spectra (KBr pellets) were measured on the Alpha Bruker FTIR instrument with scanning the entire region of 4000–400 cm^{-1} with typical resolution of 1.0 cm^{-1}. Mass spectroscopy was recorded on ES-FIGIEAN ionization mass spectrometer. Melting point was determined using an X-5A melting point measurement instrument.

2.2. Thermal analysis

Thermo gravimetric analysis (TGA) has been carried out using a Netzsch STA 409 simultaneous thermal analyzer. The samples were heated from 35 to 900 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. Flame retardancy can also be evaluated from the char residue on pyrolysis. Van Krevelen has established a linear relationship between limiting oxygen index (LOI) and char residue for halogen free polymers. The LOI was calculated by using Van Krevelen's equation. (Liu and Chiu, 2003)

$$LOI = 17.5 + 0.4(\sigma)$$

where σ is the percentage of char yield.

2.3. Biological activity

2.3.1. Microorganisms tested

Bacillus, Staphylococcus aureus and *Escherichia coli*

2.3.2. Zone inhibition

2.3.2.1. Source of microorganism. Staphylococcus (S. aureus) (ATCC 700699), *E. coli* (*E-coli*) (ATCC 104120), and *Bacillus subtlilis (Bacilius)* (ATCC 11778) were used as microorganism for the present investigation.

2.3.3. Preparation of innoculum

2.3.3.1. Preparation of innoculum. The innoculum was prepared by innoculting a loop of each test organism for 24-h culture into a sterile nutrient broth and incubated at 37 °C for 3 h, until an optical density value of 0.3 was reached in polarimeter.

2.3.3.2. Disc-diffusion method. The medium was sterilized by autoclaving a 121 °C for 15 min, cooled to 45 °C, and then poured in 20-mL quantity of Petri dish. A loop of overnight broth culture was spread evenly over whole plate with sterile cotton wool swab. The culture plates were dried in an incubator with the lid until its surface was free from visible moisture. Subsequently, 5-mm diameter sterile disc (made whatmann filter paper sterilized in UV lamp) are dipped in solutions of triaryl substituted imidazole(s); standard (ciprofloxacin hydrochloride) and control (DMSO) were placed on the surface of agar plates.

The plates were left for 1 h at room temperature as a period of pre-incubation diffusion to minimize the effects of variation in time between the applications of different solutions of triaryl substituted imidazole(s). The plates were incubated at 37 °C for 24 h and observed for antibacterial activity. The diameter of the zones of inhibition was measured for the plates in which the zone of inhibition was observed. The average area of zone of inhibition was compared with that of standard.

The biological activity of the triaryl substituted imidazole (s) was subjected to three representative numbers of pathogenic organism's viz., *E. coli, S. aureus,* and *Bacillus* respectively have been listed as Table. 1. The actual antibacterial concentration is represented by the diameter of the zone of inhibition formed around the discs impregnated with the triaryl substituted imidazoles(s).

2.4. Synthesis of 2-(4-chlorophenyl)-4, 5-diphenyl-1H-imidazole

A mixture of benzil (0.525 g; 2.5 mmol), 4-Chlorobenzaldehyde (0.35 g; 2.5 mmol), ammonium acetate (0.5 g; 6 mmol) and glycine (0.05 g) have been taken in single neck round bottom flask and heated on boiling water bath for 20 min at 80 °C temperature. The completion of the reaction was monitored by TLC. Ensuring the completion of reaction, the reaction mixture was poured into

Table 1
Thermal Analysis data of pure PVA and modified PVA.

Polymer code	T_{ON} (°C)	T_{MAX} (°C)	Char residue (%) 500 °C	600 °C	LOI
PVA	300	400	8	0	17.5
N-heterocyclic functionalized polymer	238	600	25	15	22

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