Functional Modification of Poly(vinyl alcohol) Through Phosphorus Containing Nitrogen Heterocyclic Moieties

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Received 5 October 2007; accepted 1 February 2008
DOI 10.1002/app.28629
Published online 22 August 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Functional modification of poly(vinyl alcohol) (PVA) with phosphorus containing nitrogen heterocyclic has been believed to have extensive thermal and biological applications in the area of polymers. Efforts have been taken for the synthesis of phosphorus-containing *N*-heterocyclic (5,6 member and fused ring) based PVA. The synthesized compounds were characterized using UV, FTIR, and NMR spectral studies. Thermal studies (DSC-TGA) scans display phosphorus-containing five membered and fused heterocyclic-based PVA has less thermal stability than six-membered compounds. Modified polymers infer to have excellent bacterial response against micro-organisms. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2549–2554, 2008

Key words: functional modification; PVA-nitrogen heterocyclic; thermal; spectral; antibacterial activity

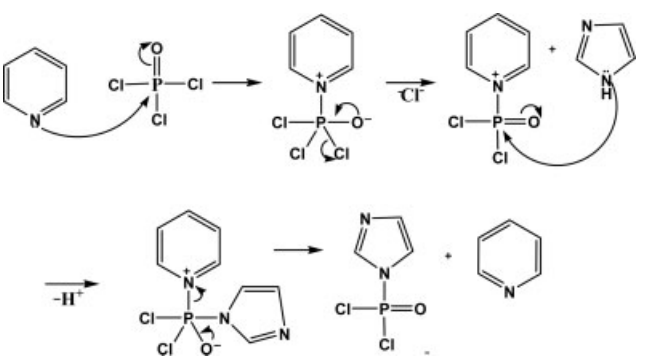
INTRODUCTION

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.[1] PVA fibers, gels, and films are potentially high performance materials because they have high tensile strength and modulus, excellent impact strength, high abrasion resistance, excellent alkali resistance, and oxygen barrier property are superior to those of any known polymer.[2–4]

Functional modification of PVA or introducing functional 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.[5–8] The synthesis of PVA that contains phosphorus and heteroaromatics in the main chain attracts the attentions of many researchers due to their peculiar characteristics viz, nonflammability, thermal stability, high melting points, and appreciable biological activities.[9–11] 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.[12]

Phosphorus-containing compounds showed their usefulness in the preparation of water-soluble polymers. Incorporation of P=O unit into PVA showed improved flame retardancy, thermal oxidative stability, and good adhesion.[13] Phosphorus-containing polymers meet the requirements of low toxicity and low smoke during combustion for environmental and health considerations. The synthesis of polymers that contains phosphorus in the main chain or side chain attracts the interest of polymer specialists. Phosphorus-containing polymers are able to increase the char during burning and thus decrease the amount of flammable zone and reduce the heat transfer from the flame to the material.[14–21] While analyzing the literature,[22] 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 is to synthesize phosphorus-containing nitrogen heterocyclic-based polymer by the reaction of PVA with nitrogen heterocyclic phosphonyl dichloride. The properties of the modified polymers such as thermal (DSC-TGA), Spectral (UV, FTIR, and NMR), and biological activities have also been investigated and compared.

Mechanism



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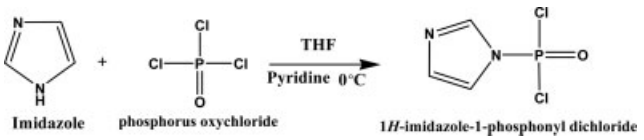


Scheme 1

EXPERIMENTAL

Materials and methods

Piperidine, piperizine, indole, imidazole, and 1,2,4-triazole were purchased from Aldrich. PVA (MW = 14,000), tetrahydrofuran (THF), dimethylformamide, and phosphorus oxychloride were purchased from SD Fine Chemicals, and solvents were purified by standard procedure. UV spectra were recorded on Shimadzu-1601; FTIR spectra were obtained from Thermonicolet 330 using KBr pellets, JEOL model GSX 400 instrument was used to record the NMR spectra. SDT Q600 V8.0 build 95 system was used for thermal studies at a heating rate of 10°C/min under nitrogen atmosphere.

TABLE I
Product Name and Notations

S.No	Product name	Notation
1	Poly(divinyl 1H-imidazol-1-yl-1-phosphonate)	IM-PDP
2	Poly(divinyl 1H-1,2, 4-triazol-1-yl-1-phosphonate)	TZ-PDP
3	Poly(divinyl piperidin-1-yl-1-phosphonate)	PD-PDP
4	Poly(tetravinyl piperazin-1,4-diyl-1, 4-bis(phosphonate))	PZ-PDP
5	Poly(divinyl 1H-indol-1-yl-1-phosphonate)	IN-PDP

TABLE II
Reaction Sequence and Product Code

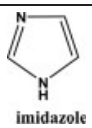
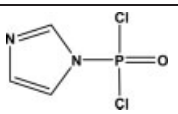
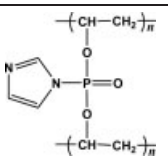
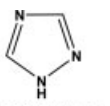
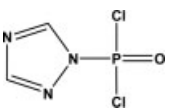
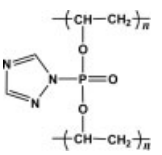
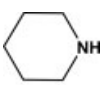
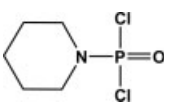
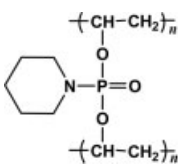
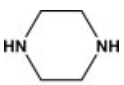
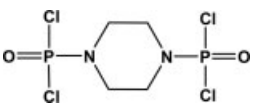
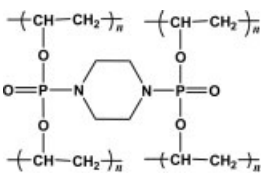
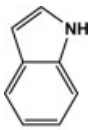
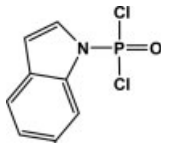
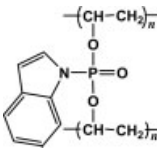
S.No	*N*-Heterocyclic compounds	*N*-Heterocyclic phosphonyl dichloride (Stage I)	Phosphorus containing *N*-heterocyclic poly(vinyl alcohol) (Stage II)	Product code
1	 imidazole			IM-PDP
2	 1*H*-1,2,4-triazole			TZ-PDP
3	 piperidine			PD-PDP
4	 piperazine			PZ-PDP
5	 Indole			IN-PDP

TABLE III
Product Description

S. No.	Product code	Stage I		Stage II		
		Yield (%)	Solubility	Yield (%)	Solubility	Appearance
1	IM-PDP	87	DMF	85	Water	White and waxy
2	TZ-PDP	84	THF and DMF	75	Water	White and waxy
3	PD-PDP	82	DMF	80	Water	White and waxy
4	PZ-PDP	75	THF and DMF	78	Water	White and waxy
5	IN-PDP	88	THF and DMF	82	Water	Brown and waxy

Preparation of *N*-heterocyclic phosphonyl dichloride moieties

About 1 mmol (0.068 g) of imidazole and 2 mmol (0.153 g) of phosphorus oxychloride were dissolved separately in 20 mL of THF each and added slowly one over the other using an additional funnel with constant stirring for 15 min at 0°C in the presence of catalytic amount of pyridine. The reaction was continued for 3 h. Then the reaction mixture was filtered, and the solvent was evaporated to get 1H-imidazole-1-phosphonyl dichloride. The progress of the reaction was monitored by TLC and separated by column chromatography. The same procedure was adopted for 1,2,4-triazole, piperidine, piperazine, and indole to get various *N*-heterocyclic phosphonyl dichlorides, respectively, are displayed in Table II and Scheme 1.

Note: for piperazine, 4 mmol of phosphorus oxychloride was taken, because it reacts with both the acidic protons.

Functional modification of PVA using *N*-heterocyclic phosphonyl dichloride moieties

N-Heterocyclic phosphonyl dichloride (1 mmol) and PVA (6 mmol) were dissolved in 50 mL of dry dimethylformamide at 90°C for 12 h with constant stirring. Then the solvent was removed under reduced pressure, and the resulting product was dried at 50°C using vacuum oven. The product name and notations are given in Table I, and their descriptions are displayed in Tables II and III.

Biological activity

Source of microorganism

Staphylococcus aureus (*S. aureus*) (ATCC 700699), *Escherichia coli* (*E. coli*) (ATCC 10412), and *Bacillus subtilis* (*Bacilius*) (ATCC 11778) were used as micro-organisms for the present investigation.

TABLE IV
UV Absorption Data

	IM-PDP	TZ-PDP	PD-PDP	PZ-PDP	IN-PDP
UV (λ_{max}) (nm)	216	214	248	222	215

Preparation of innoculum

The innoculum was prepared by innoculating 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.

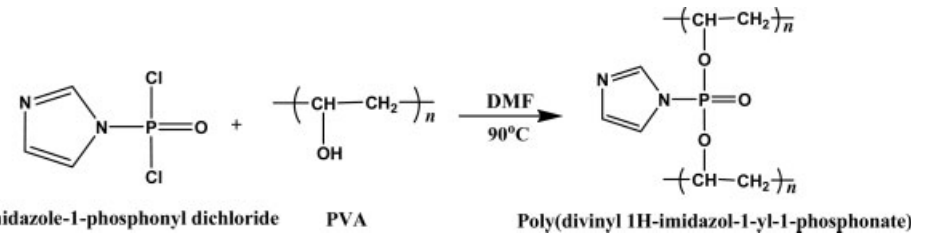
Disc-diffusion method

The medium was sterilized by autoclaving at 121°C for 15 min, cooled to 45°C, and then poured in 20-mL quantity of Petri dish. A loopful 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 discs (made from Whatmann filter paper sterilized in UV lamp) are dipped in solutions of modified polymers; 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 preincubation diffusion to minimize the effects of variation in time between the applications of different solutions of modified polymers. 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.

TABLE V
FTIR Information of Modified Polymers

S. No.	Product code	P=O stretch (cm^{-1})	P—N stretch (cm^{-1})	P—O—C stretch (cm^{-1})
1	IM-PDP	1254.92	1103.06	1062.99
2	TZ-PDP	1256.75	1103.84	1025.42
3	PD-PDP	1249.90	1102.81	1018.45
4	PZ-PDP	1255.58	1099.35	1020.22
5	IN-PDP	1255.38	1101.64	1063.36



Scheme 2

RESULTS AND DISCUSSIONS

Spectral studies

Table IV deals with the UV-spectral studies of all modified polymers. It shows that the λ_{max} value in the range of 214–248 nm, which corresponds to $-$ *. Five membered and fused heterocyclic-modified PVA are around 214 nm. Six-membered heterocyclic modified samples display higher values than the other in the range of 222–248 nm.

Table V summarizes FTIR information on modified polymers. The formation of the *N*-heterocyclic phosphonyl dichloride were confirmed by disappearance of N—H stretching and appearance of P—N and P=O stretching. P—Cl stretching for the all-synthesized compounds was shown around 585 cm^{-1}. Similar results were observed by Hamciuc et al.[14] for their research report on kinetics of thermal degradation in nonisothermal conditions of some phosphorus-containing polyesters and polyesterimides.

Phosphorus-containing *N*-heterocyclic (5, 6 member and fused ring) modified PVA were presented in Scheme 2. Disappearance of P—Cl stretching and formation of P—O—C stretching confirm the formation of the product as given in Table V.

The product IM-PDP shows the ^{13}C NMR signals at 127, 122, and 136 ppm and corresponds to imidazole carbons. IN-PDP shows the NMR signals at 102, 111, 119, 120, 122, 124, 128, and 136 ppm responsible for indole carbons. A singlet at 45 ppm for PZ-PDP reveals the same environment of four carbon atoms. For PD-PDP, 25.6, 27.2, and 45.9 ppm relates piperidine carbons. The NMR spectrum of TZ-PDP at 151 ppm represents the same environment of two carbons of triazole. Singlet of 74 and 30 ppm corresponds to CH and CH_2 of PVA, respectively. ^{31}P NMR shows a singlet in the range of 1.725–2.860 ppm from IM-PDP to IN-PDP. Hence, the ^{13}C NMR and ^{31}P NMR results in supporting the structure of the compounds.

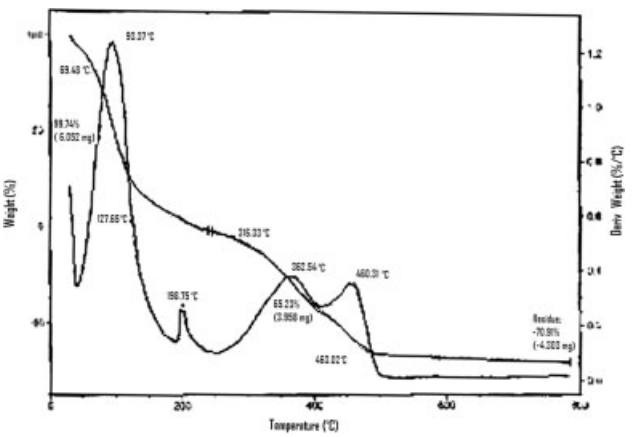


Figure 2 DSC-TGA scan of TZ-PDP.

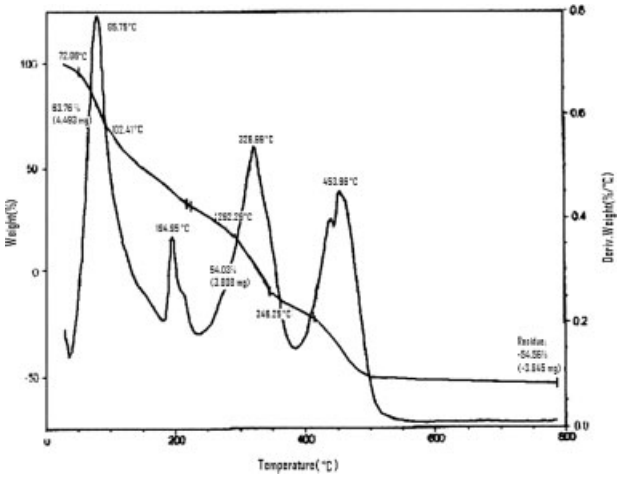


Figure 1 DSC-TGA scan of IM-PDP.

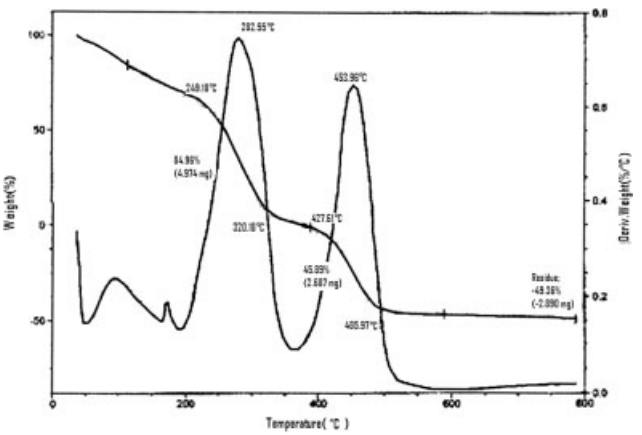


Figure 3 DSC-TGA scans of PD-PDP.

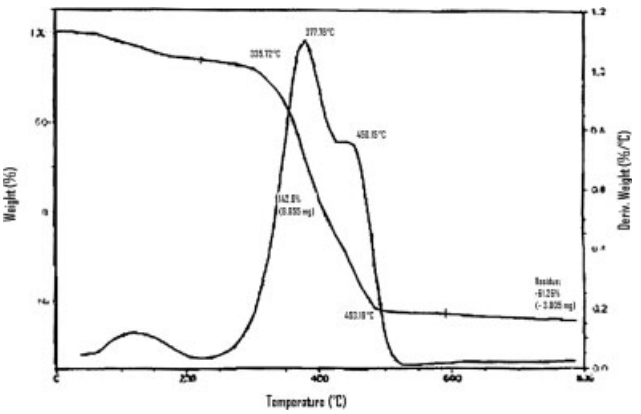


Figure 4 DSC-TGA scan of PZ-PDP.

Thermal studies

The thermogravimetric analysis is one of the commonly used techniques for rapid evaluation of thermal stability of different materials. It also indicates the decomposition of polymers at various temperatures. Figures 1–5 show the TGA/DSC scanned report on IM-PDP, IN-PDP, PZ-PDP, PD-PDP, and TZ-PDP contents from 0 to 800°C at the heating rate of 10°C/min under nitrogen atmosphere. The sample weight was taken around 5.8–7.2 mg. The slope of the curve indicates the rate of weight loss of the material, and the rate of weight loss decreases with decreasing value of slope of the curve. Analyzing the recorded thermograms, we notice that the degradation occurs in different stages with various weight losses in the molecule.

The thermal stability of 5% initial weight loss of PVA (MW = 1, 50,000) occurs at 270°C, which may be higher than the modified PVA when the thermal degradation just occurs.[23] Tables VI and IX describe the results of thermogravimetric analysis. Around 15% weight loss occurs at 72°C for IM-PDP, 100°C for IN-PDP, 110°C for PD-PDP, and 69°C for TZ-PDP, respectively. This may be due to the less

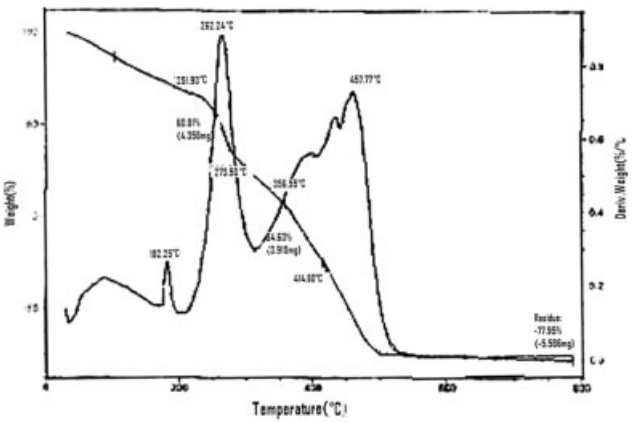


Figure 5 DSC-TGA scan of IN-PDP.

TABLE VI
Thermogravimetric Analysis Data of Modified Polymers

	Percentage of Weight loss			
Product code	0–15	46–60	61–75	76–90
IM-PDP	72°C	292°C	346°C	500°C
TZ-PDP	69°C	127°C	316°C	463°C
PD-PDP	110°C	315°C	427°C	486°C
PZ-PDP	335°C	–	–	453°C
IN-PDP	100°C	356°C	414°C	500°C

strength of the phosphorus bonds (P-O, P-N, and P-O-C) in polymers at relatively low temperature region than the ordinary polymer chain.[24] But in the case of PZ-PDP, 15% weight loss occurs at 335°C. This may be due to the presence of four modified vinyl linkages attached to PZ-PDP. This shows that the PZ-PDP has more thermally stable than other modified heterocyclic moieties. Based on the results of TGA, the order of decreasing thermal stability are as follows:

PZ-PDP > PD-PDP > IN-PDP > IM-PDP > TZ-PDP

Differential scanning calorimeter

The initial decomposition temperature (T^1_{max}) of all the compounds was evaluated and given in Tables VII and IX. Five-membered IM-PDP and TZ-PDP have four maxima in the range of 85–460°C. Three maxima were observed for fused IN-PDP in the range of 93–457°C, whereas two maxima were observed for six-membered PZ-PDP and PD-PDP in the range of 282–453°C. It was observed that PZ-PDP results in T^1_{max} at 377.78°C, which may be due

TABLE VII
Differential Scanning Calorimeter (DSC) Data of Modified Polymers

Product code	T^1_{max} (°C)	T^2_{max} (°C)	T^3_{max} (°C)	T^4_{max} (°C)
IM-PDP	85.75	194.95	326.99	453.93
TZ-PDP	93.37	198.75	362.54	460.31
PD-PDP	282.55	453.96	–	–
PZ-PDP	377.78	450.15	–	–
IN-PDP	182.25	262.24	457.77	–

T^1_{max} is initial decomposition temperature; T^2_{max} the second decomposition temperature; T^3_{max} the third decomposition temperature; T^4_{max} the final decomposition temperature.

TABLE VIII
Biological Studies on Modified Polymers

Compounds	*Escherichia coli* (mm)	*Bacillus* (mm)	*Staphylococcus aureus* (mm)
IM-PDP	–	–	0.9
TZ-PDP	0.5	0.8	–
PZ-PDP	0.9	0.7	–
PD-PDP	–	0.8	–
IN-PDP	–	0.7	–

TABLE IX
Comparative Study

Characterization	IM-PDP	TZ-PDP	PD-PDP	PZ-PDP	IN-PDP
Thermal study					
TGA (around 15% weight loss) at °C	69	72	110	220	100
DSC (T_{max}) °C	85.75	93.37	282.55	377.78	182.25
Biological study					
Escherichia coli	−	+	+	−	−
Bacillus	−	+	+	+	+
Staphylococcus aureus	+	−	−	−	−

to the presence of four bulky PVA chain in the molecule.

Biological studies

The biological activity of the five investigated systems (IM-PDP, TZ-PDP, PD-PDP, PZ-PDP, and IN-PDP) was tested against a representative number of pathogenic organisms (*E. coli*, *S. aureus*, and *Basillus*).

The monitoring of antibacterial activity is usually performed by the determination of the MIC,[25] the smallest amount of the agent that inhibits the multiplication of the pathogen. The actual antibacterial concentration is represented by the diameter of the zone of inhibition formed around the discs impregnated with the modified polymer. Therefore, it is found that the MIC for all the systems having certain activity are presented in Tables VIII and IX. IM-PDP was considered to be good for *S. aureus*. PZ-PDP and TZ-PDP were excellent activity against both *E. coli* and *Basillus*. PD-PDP and IN-PDP showed considerable response against *Basillus*.

The improved bacterial activity was due to the incorporation of phosphorus-containing different types of heterocyclic moieties into the PVA. Based on the obtained results from biological studies, the order antibacterial activity was given as

PZ-PDP > TZ-PDP > IM-PDP > PD-PDP > IN-PDP.

CONCLUSIONS

Based on the careful analyses of the present investigation, the following conclusions were made:

1. Biologically active phosphorus-containing heterocyclic-based functionally modified PVA was synthesized.
2. Formation of compounds was confirmed by using TLC, FTIR, and NMR studies, respectively.
3. DSC-TGA scans displays phosphorus-containing five membered and fused heterocyclic-based modified PVA is thermally less stable than six membered.
4. IM-PDP was considered to be good for *S. aureus*. PZ-PDP and TZ-PDP have excellent activity against both *E. coli* and *Basillus*. PD-PDP and IN-PDP showed considerable response against *Basillus*.

We thank VIT University for providing laboratory facilities and VIT-TBI for recording spectral data.

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