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THERMAL STABILITY OF SOME BIOLOGICALLY ACTIVE FUNCTIONALLY MODIFIED POLY (VINYL ALCOHOL)

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ABSTRACT

Polymers form a very important class of materials without which the life seems very difficult. It has been believed that the antimicrobial activity of the compound mainly due to the presence of heteroatoms like nitrogen and phosphorous as similar to the naturally occurring polymers viz., DNA, proteins etc., incorporation of heterocyclic functionality to the synthetic polymers found to exhibit the biological activity to the existing polymers than their unmodified polymers. Based on the literature, the present work have been designed to have benzodiazepine functionalized vinyl polymers like Poly (vinylalcohol). Functionally modified PVA have been characterized by spectral (FTIR, ^{1}H-NMR and ^{13}C-NMR), thermal (TGA) analysis. Functionally modified PVA have also been subjected into antimicrobial studies. Results of the investigation reveals that the functionally modified PVA exhibited good thermal stability and moderate antimicrobial action against unmodified PVA.

KEYWORDS: Chalcones; benzodiazepines; functional modification; thermal stability; antimicrobial activity.

1. INTRODUCTION

Polymeric flame retardants (FRs) have been very much attractive field due to the large applications towards the fire retardant activity. Incorporation of a polymeric flame retardants, the physical and mechanical properties of the polymer are considerably changed. It can helps to decrease the diffusion in the polymeric systems and consequent risk of environmental contamination. Polydibromostyrene and polyphosphazenes are popular FRs among the all flame retardants.[1,2] In a broad sense, all the fire-resistant polymers can be used as polymeric

flame retardants must be blended with some other organic flame retardant compounds to enhance their fire retardancy. Finally, the ultimate and convenient way to reduce the polymer flammability is to incorporate the phosphorus and nitrogen containing heterocycles with polymeric backbone by chemical methods. Incorporation of P=O unit into PVA showed improved flame retardancy, thermal oxidative stability and good adhesion.[3]

Phosphorus containing organophosphorus compounds, in general used in combination with nitrogen to exhibit flame retardant applications. These FRs are commonly known as char formers due to thermal decomposing process to produce phosphoric acids. These acids react with components in the substrate to eventually form a char which protects the substrate from further pyrolysis. The presence of nitrogen in natural polymers appears to exert some degree of flame retardance, as shown by the relatively low flammability of wool, silk and leather.[4] A number of nitrogen-containing organic compounds are used as reactive flame retardants for certain polymers. These include triazines, isocyanates, urea, guanidine, and cyanuric acid derivatives.[5]

Polymeric materials have widely been used for many applications. Vinyl polymer is one among the polymers usually encountered in day to day life. It has been well-known in numerous applications viz., computer applications, automobiles, biomedical applications,[6] aero components, toys and other numerous household appliances. Although vinyl polymers has huge applications, it suffers from high flammability which limits its use for many desirable applications. The most common method to impart fire retardance vinyl polymers is the use of flame retardant additives such as halogenated aromatics or organic and inorganic phosphorus compounds. Additive systems have the disadvantages of promoting undesirable changes in physical and mechanical properties of the polymer and found to have poor durability in long term use.[7] 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.[8-10]

In recent years, Phosphorus-based polymers have widely been studied as they exhibit very constructive and motivating properties. Phosphorus-containing organic polymers can be employed for a wide range of technological applications. For instance, they are extensively used in industry as binding metals, dispersants, corrosion inhibiting as well as to prevent deposit formation. Apart from the industrial usage, it serves in biomedical field as they are

biodegradable, blood compatible, show reduced protein adsorption and lead to strong interactions with dentin, enamel or bones. Phosphorus-containing polymers are able to increase the char while burning, which decreases the amount of flammable zone and reduce the heat transfer from the flame to the material.[11-13]

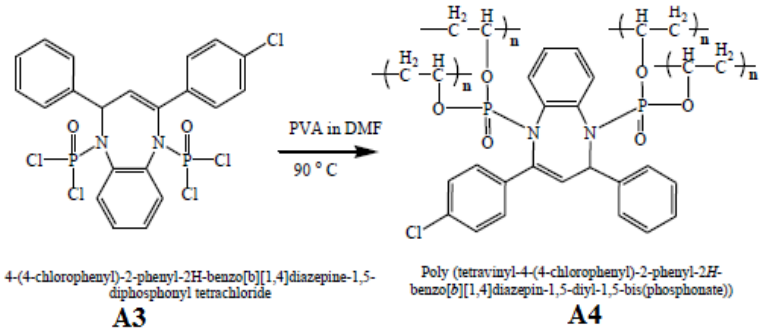
Hence, the work has been designed to increase the thermal stability and flame retardant activity of PVA by incorporating phosphorus and nitrogen containing organic groups through N-P linkage. The N-P linkages, in general, believe to have most stable as they were found in natural polymers like DNA and RNA.

2. MATERIALS AND METHODS

Commercially available AR grade chemicals with high purity were used. PVA, silica gel and $POCl_3$ were purchased Merck and used for the synthesis of functionally modified PVA. The solvents like THF, DMSO and ethanol were purified by according to standard procedure. Fourier-transform infrared spectra were obtained as KBr disks on Shimadzu spectrometer. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectra were obtained using Bruker Advanced 300MHz NMR spectrometer, using TMS as internal standard and $CDCl_3$ used as a solvent. Thermogravimeric analysis (TGA) of the samples was carried out using SEIKO SII, Model 6200 TGA/DTG, USA, with heating rate for 20°C per minute in nitrogen atmosphere. The weight losses at different stages were analysed. 1-6 mg of the sample was taken for analysis and TGA scan was run upto 720°C. Anti-bacterial activity have been studied using disc diffusion method for a series of selected number of pathogens viz., *Staphylococcus aureus, Streptococcus fecalis, Pseudomonas aeruginosa and Escherichia coli*. Similarly, the disc diffusion method has also been used for antifungal activity, against the selected fungi namely, *Aspergillus niger, Aspergillus flavus, Penicillium sps, Fusarium* sps.

2.1. Procedure for the Synthesis of Poly (tetravinyl-4-(4-chlorophenyl)-2-phenyl-2H-benzo[b][1,4] diazepin -1,5-diyl-1,5-bis(phosphonate)) (A4)

4-(4-chlorophenyl)-2-phenyl-2H-benzo[b][1,4]diazepine-1,5-diphosphonyl tetrachloride **(A3)** (0.494 g, 1 mmol) and Poly (vinyl alcohol) (PVA) (20.4 g, 12 mmol) were dissolved in 50 ml of dry dimethylformamide (DMF) at 90°C for 12 hours with constant stirring. Then, the solvent was removed under reduced pressure the resulting in pale yellow crystalline polymer was dried at 50°C using vacuum oven **(scheme 2.1)** and the pure product has been characterized by FTIR, ^{1}H NMR and ^{31}P NMR spectral technique.



Scheme 2.1. Synthetic route for the formation of functionally modified PVA derivative

3. RESULTS AND DISCUSSION

3.1. Spectral data for the compound A4

Poly (tetravinyl-4-(4-chlorophenyl)-2-phenyl-2H-benzo[b][1,4] diazepin -1,5-diyl-1,5-bis(phosphonate)): Dark brown granulars; FTIR(KBr,cm^{-1}): 3429 (O-H), 2924 (Ar-C-H), 1332 (P=O), 1198 (P-N), 1097 (P-O-C);^{1}H NMR ($CDCl_3$, 400MHz) δ ppm: 8.19-7.95 (13H,m,Ar-H), 7.91-7.89 (1H,d), 3.89-3.83 (1H,d), 3.37(-OH,s),2.50 (1H,s), 1.49-1.38 (2H,dd); ^{13}C NMR ($CDCl_3$, 100MHz) δ ppm: 36.6, 45.8, 68.2, 111.4,125-128, 151.8. ^{31}P NMR δ ppm: 2.60, 2.97.

In FTIR spectra of A4 (Fig-3.1), considerable decrease in the area of the –OH peak reveals that the hydroxyl groups of the polymer which decreases after modification. The disappearance of P-Cl stretching at 565 cm^{-1} and formation of P-O-C stretching at 1097.50 cm^{-1} have confirmed the formation of the **A4.** The existence of P-N and P=O stretching at 1198.40 and 1332.81 cm^{-1} has also been supported the structure of **A4.** Somasundaran, *et.al.*, (2014) have also noticed the similar stretching frequencies for their modified PVA.[14]

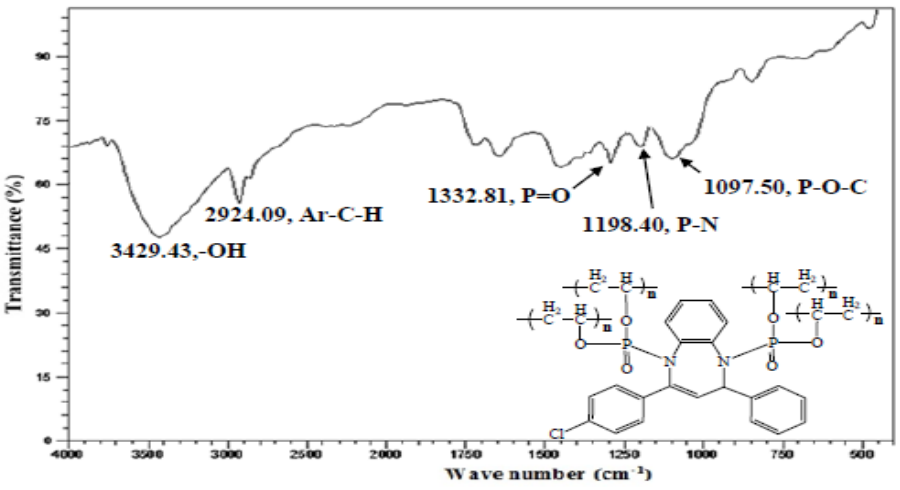


Figure 3.1. FTIR spectrum of compound A4.

The ^{1}H NMR spectra of compound A4 have shown in Fig-3.2, The peaks at δ ppm 7.91-7.89 and 3.89-3.83 values for Benzodiazepine protons and peaks at 7.95-8.19 δ ppm for aromatic ring protons. A doublet of doublet peak at 1.49-1.38 δ ppm, the singlet peak at 2.50 δ ppm associated with CH_2 and CH protons of PVA respectively.

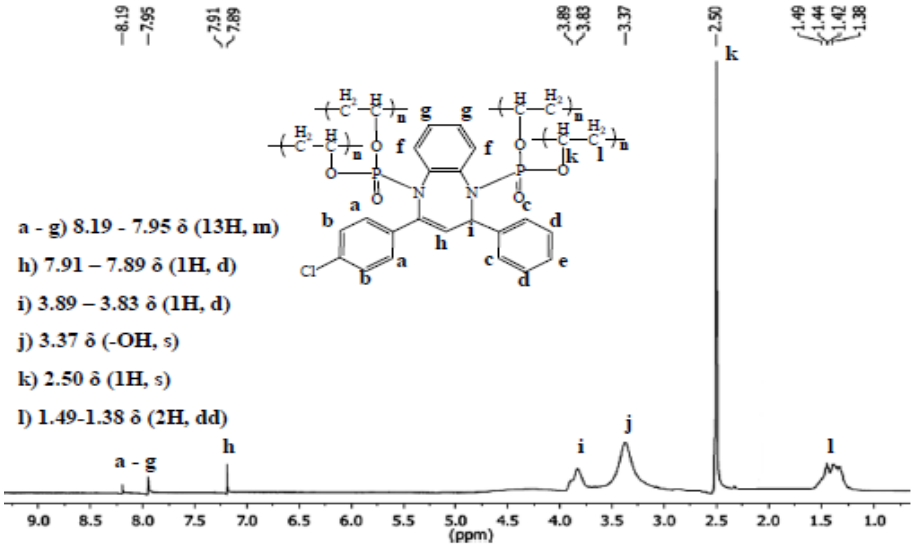


Figure 3.2. ^{1}H NMR spectrum of compound A4.

Fig-3.3 showed the ^{13}C NMR spectrum of compound **A4.** The peaks appeared at 36.6, 68.2 δ ppm related to CH_2 and CH carbons of the PVA respectively. Further, the peaks at 45.8, 111. 4,151.8 δ ppm due to –CH carbon and ethylenic carbons labelled as 'b,d,e' respectively.

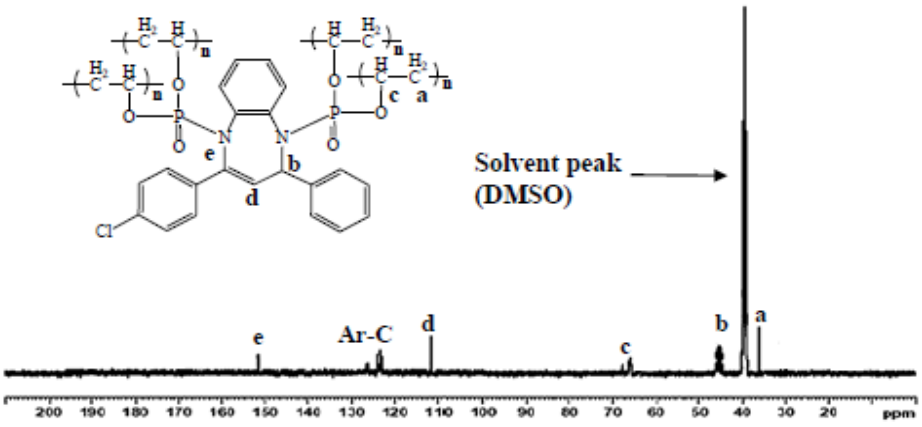


Figure 3.3. ^{13}C NMR spectrum of compound A4.

Fig-3.4 represents the ^{31}P NMR spectrum of compound **A4.** The two peaks at 2.60, 2.97 δ ppm confirmed the presence of two different environmental phosphorus in target compound **A4.**

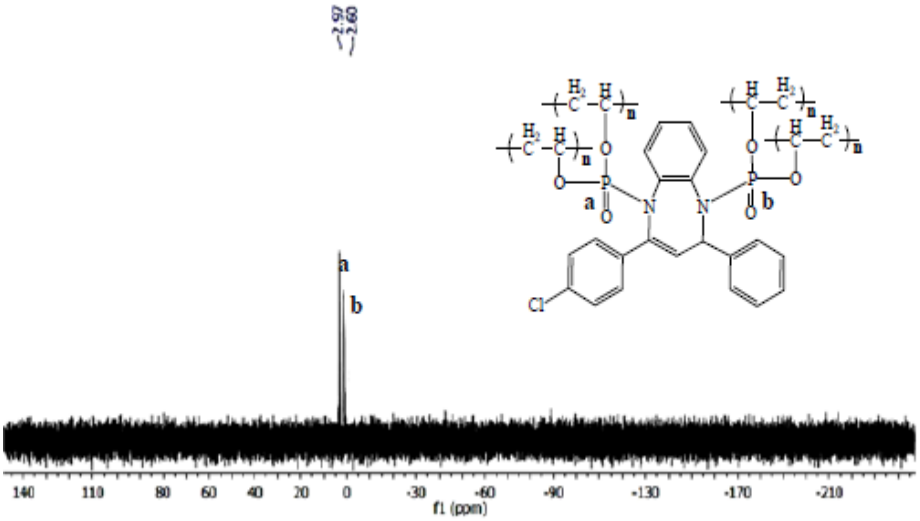


Figure 3.4. ^{31}P NMR spectrum of compound A4.

3.2. Thermo gravimetric analysis of compound A4

Thermal Gravimetric Analyser measures the change in the mass of a sample as on when a sample is heated, cooled or held at a constant (isothermal) temperature. Functionally modified PVA **A4** has three stage of disintegration (Fig-3.5). At 10-15% initial weight loss might be due to loss of phenyl groups were identified at 280ºC in benzodiazepine moiety**.** 45-60% weight loss was noticed at 340ºC. This can be related to the cleavage of four modified vinyl linkages attached to two nitrogen of organophosphorus benzodiazepine**.** 61-90% weight loss was observed at 490ºC due to deformation of organophosphorus moiety.[15] (Tagawa, (1984)).

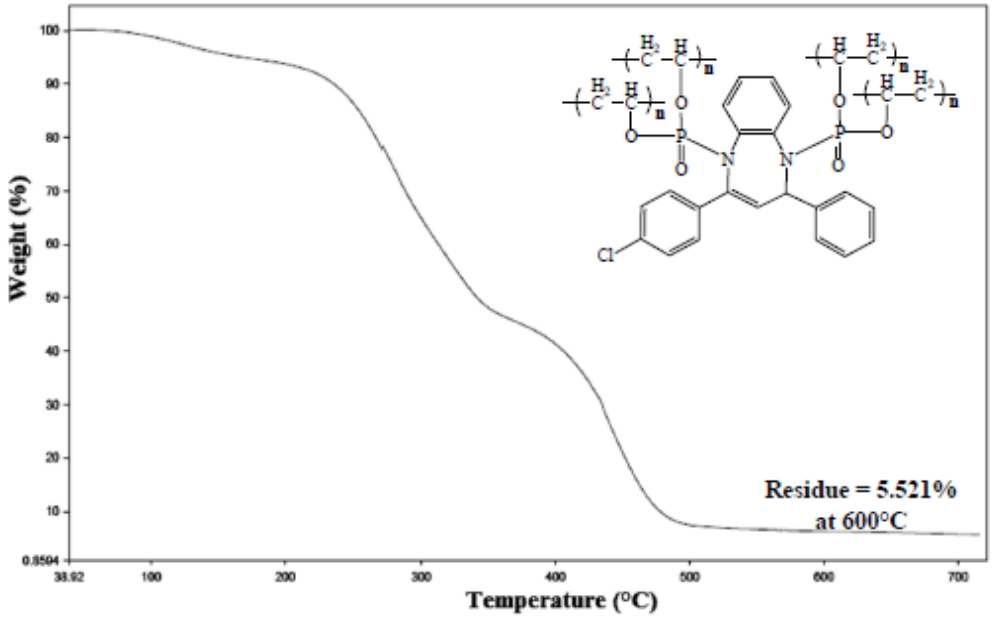


Figure 3.5. TGA curve of compound A4.

This implies that heterocyclic modified PVA has good flame retardant compound. This behaviour was mainly due to the presence of P-N, P-O-C bonds, and heterocyclic compounds in the modified polymers. These structures act as weak links and they were highly susceptible to chain scission during thermal degradation. A similar fashion was sensed by Chiang, *et.al.*,(2002).[16] According to their report the excellent thermal stability and flame retardancy was due to the presence of N-P bond formation.

3.3. Biological activity

3.3.1. Antibacterial activity of functionally modified PVA (A4) and pure PVA

As per the study on ZOI for the synthesized compound (A4) found to have certain activity against the pathogenic organisms. **Table 3.1** summarised the consolidated ZOI values of organophosphorus benzodiazepine containing modified PVA with pure PVA. According to this table, target compound found to have excellent activity towards *Staphylococcus aureus*. and *Escherichia coli* than pure PVA (Fig-3.6).

Table 3.1. Anti-bacterial activity values of modified PVA (A4) with pure PVA.

Compound Code	Gram-positive				Gram-negative			
	Staphylococcus aureus		Streptococcus faecalis		Pseudomonas aeruginosa		Escherichia coli	
	Zone Of Inhibition (ZOI)							
	mm	%	mm	%	mm	%	mm	%
PVA	7	26.9	6	25.0	6	24.0	7	25.9
A4	8	30.8	6	25.0	4	16.0	9	33.3
Control	-	-	-	-	-	-	-	-
*Ciprofloxacin	26	100	24	100	25	100	27	100

(*Activity of Ciprofloxacin considered as 100% inhibition against selected pathogens).

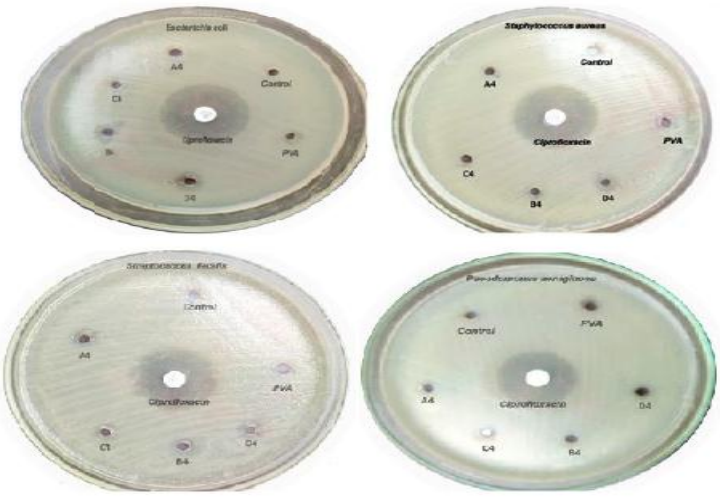


Figure-3.6. Antibacterial activity of compound A4 and PVA.

3.3.2. Antifungal activity of functionally modified PVA (A4) and pure PVA

From the careful observation of Zone of inhibition values of compound A4 and PVA (Table-3.2), compound A4 found to have nice anti-fungal activity against selected species namely, Aspergillus niger, Aspergillus flavus, Penicillium ps, Fusarium sps through Zone Of Inhibition method as shown in the Fig-3.7.

Table 3.2. Anti-fungal activity values of modified PVA (A4) with unmodified PVA.

Compound Code	*Aspergillus niger*		*Aspergillus flavus*		*Penicillium sps*		*Fusarium sps*	
	Zone Of Inhibition (ZOI)							
	mm	%	mm	%	mm	%	Mm	%
PVA	8	61.5	8	57.1	10	66.7	10	62.5
A4	7	53.8	11	78.6	11	73.3	9	56.3
Control	-	-	-	-	-	-	-	-
*Amphotericin B	13	100	14	100	15	100	16	100

(*Activity of Amphotericin B considered as 100% inhibition against selected pathogens).

Figure-3.7 Antifungal activity of compound A4 and PVA.

4. CONCLUSION

Finally, the functionally modified PVA derivative was achieved through the creation of N-P bond and it was confirmed by various spectral techniques namely, FTIR, ^{1}H NMR, ^{13}C NMR and ^{31}P NMR. The enhanced thermal stability was also observed from TGA analysis for the compound A4 than PVA. The antibacterial and antifungal activities were also found for the

compound A4 was excellent against the selected pathogens. Moreover, the expected modification to PVA were successfully observed and found the increased thermal and biological activities due to the incorporation of biologically active organophosphorus benzodiazepine compound.

5. ACKNOWLEDGEMENT

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REFERENCES

1. Mark, J.E., Allcock, H.R., and West, R., Inorganic Polymers, Prentice Hall, New Jersey, 1992.
2. Zingde, G., In ANTEC Technical Conference Proceedings, 1996; 54(3): 3004.
3. Vld-Bubulac, T.; Hamciuc, C.; Petreus1, O.; Bruma, M. Proceeding of the 8th Polymers for Advanced Technologies International Symposium, Budapest, Hungary, September, 2005; 13–16.
4. Horacek, H., and Grabner, R., Polym. Degrad. and Stability, 1996; 54: 205.
5. Horacek, H., and Grabner, W., Makromol. Chem., Macromol. Symp., 1993; 74: 271.
6. Christie M. Hassan.,Nikolaos A. Peppas., Advances in Polymer Science, 2000; 154.
7. Somasundaran, D., and Guhanathan, S., *Der Chemica Sinica*, 2014; 5(6): 90.
8. Sakurada, I. In Polyvinyl Alcohol Fibers; Lewin, M., Ed.; Marcel Dekker: New York, 1985.
9. Martin, F. L. In Encyclopedia of Polymer Science and Technology; Mark, H. F., Bikales, N. M., Menges C. G., Kroschwitz, J.I., Eds.; Wiley: New York., 1985.
10. Masuda, M. In Polyvinyl Alcohol-Development; Finch, C. A., Ed.; Wiley: New York, 1991.
11. Hamciuc, C.; Bubulac, T. V.; Petreus, O.; Lisa, G. Eur. Polym. J., 2007; 43: 980.
12. Wang, Y.-Z.; Chen, X.-T.; Tang, X.-D. J. Appl. Polym. Sci., 2002; 86: 1278.
13. Liu, Y. L.; Tsai, S. H. Polymer, 2002; 43: 5757.
14. Somasundaran, D., Elumalai, S., and Guhanathan, S., *IJACSA*, 2(4): 2014.
15. Tagawa, H., *Thermochimica Acta*, 1984; 80: 23.
16. Chiang, C. L., and MA, C. C., *Eur. Polym. J.*, 2002; 38: 2219.