IJCPS Vol. 5, No. 3 , May-Jun 2016
www.ijcps.org
ISSN:2319-6602
International Journal of Chemical and Physical Sciences

Thermal and Microbial Studies of Copolymers of Acrylonitrile/ Acrylamide/ Vinyl Acetate of N-Substituted Maleimide

JYOTI CHAUDHARY[1], SWATI PUROHIT[2], SUMAN JINGER[3], HARSHDA JOSHI[4]

[1,2,3]Department of Polymer Science, M.L.S.U.,Udaipur (Raj.) India
[4]Department of Biotechnology, M.L.S.U.,Udaipur (Raj.) India
E-Mail: purohit.swati3@gmail.com

Abstract

The N-(pyridine-2-yl)maleimide (PYMI) and it's homo and copolymers have been synthesized and characterized by FT - IR and ^{1}H- NMR spectroscopic methods. Copolymers (C-PYMI) with various proportions of N-(pyridine-2-yl)maleimide (PYMI) and Acrylonitrile [AN] were prepared by free radical polymerization in tetrahydrofuran (THF) using 2,2'-azo-bis-isobutyronitrile (AIBN) as an initiator at 70 ± 2°C. The nine copolymer samples were synthesized from different feed ratio of comonomers. The monomer reactivity ratio r_{PYMI} and r_{AN} were determined by Finemann Ross method. The investigated homo and copolymers showed solubility in Polar solvents like THF, DMF, Dioxane, acetone, chloroform, and ethyl acetate. Thermal behavior of homopolymer and copolymers were evaluated by TGA and DSC. The molecular weights were determined by GPC. The Antimicrobial activity of synthesized homopolymer and copolymers were screened and they showed excellent antimicrobial activity.

Keywords: Homo and Copolymerization, AIBN, Acrylonitrile, TGA, GPC, F-R Method.

Introduction:

The development of highly thermal stable and biological active polymers is on the rise to meet the growing demand of rapidly evolving high technological field [1].N-Substituted maleimide have received growing interest because of their excellent thermal properties, low dielectric constant and though mechanical properties[2]. Maleimide polymers have good environment stability and outdoor applications, where environmental conditions influence their performance [3].

Maleimide unit effectively enhance both glass transition temperature (Tg) and thermal degradation temperature of the copolymer. Thus *N*-phenylmaleimide polymers are used in some electro-optical applications which require the improvement of the thermal stability, processability, electro-optical coefficients, and optical loss [4].

Due to versatile properties of maleimide we synthesized the copolymer of maleimide with vinyl monomer containing different functional group. Copolymers containing acrylamide derivatives are potentially useful as carriers for gene delivery. Polyacrylamide is used in agriculture or water treatment, paper making and in molecular biology applications as a medium for electrophoresis of proteins and nucleic acids. Copolymers of acrylonitrile are elastomers and find their applications as petroleum and mineral –oil resistant rubbers [5].Along with polymer vinyl acetate used in adhesives, lacquers and in manufacture of gramophone records.

In this paper, we have reported the synthesis, characterization of PYMI (N-(pyridine-2-yl) maleimide) monomer, homo and copolymers with Acrylonitrile , Vinyl acetate, Acrylamide.

Experimental Work

Materials and Methods

All chemicals used in the synthesis are of reagent grade and are used without further purification. C, H, N elemental analyses were performed on a Perkin Elmer 240c elemental analyzer. Infrared spectra were recorded in the form of KBr pellets on a FT-IR Perkin-Elmer spectrometer.^{1}H-NMR spectra were measured on BRUKERAVENCE II 400 MHz NMR spectrophotometer. TG analyses were carried out on Perkin Elmer Pyris-1 thermal analyzer.

Synthesis

Synthesis of PYMI (N-(pyridine-2-yl)maleimide) from maleic anhydride and 2-amino pyridine according to reported method [6]. Synthesis process of PYMI [N-(pyridine-2-yl)maleimide] are shown in the following reaction scheme. Monomer (PYMI) was homo and copolymerized with Acrylonitrile (AN), Vinyl acetate (VA), Acrylamide (AM) are Copoly-N-(pyridine-2-yl)maleimide -co-AN (PYMI-co- AN) ,Copoly-N-(pyridine-2-yl)maleimide -co-VA (PYMI-co- VA),Copoly- N-(pyridine-2-yl)maleimide -co-AM (PYMI-co-AM) shown below.**[Scheme 1]**

Result and discussion

Density of synthesized monomer and polymers were determined by using density bottle at room temperature. **[Table1]**

Viscosity of synthesized monomer and polymers were determined by using Ubbelhode viscometer at room temperature.**[Table 1]**

The number average molecular weights of the polymers were evaluated by GPC.The number average molecular weight (Mn), weight average molecular weight (Mw) and polydispersityindex (Mw/Mn) are shown below. **[Table 1]**

Polymer Code	**ρ(g/cm^3)**	**η(dl/g)**	**M_W**	**M_n**	**PDI (Poly Dispersity Index)**
H-PYMI	0.5254	0.3697	1096	786	1.3945
PYMI-co-AN	0.3703	0.1651	1113	765	1.456
PYMI-co-VA	0.3172	0.1311	995	521	1.9097
PYMI-co-AM	0.4715	.2954	1189	859	1.3841

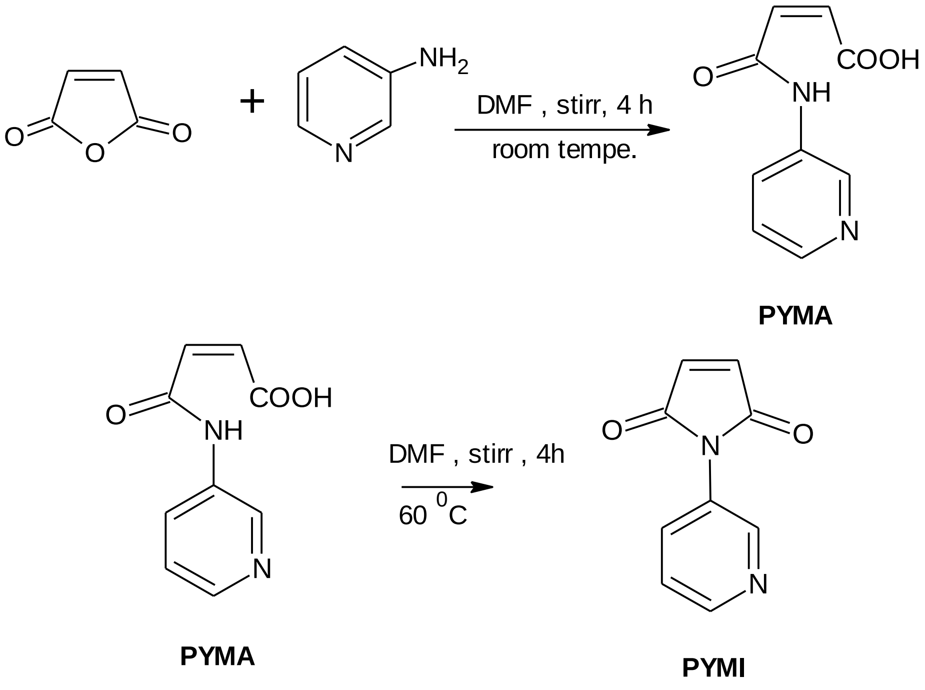
Table 1: Density, Intrinsic Viscosity, Molecular Weight of Homopolymer and Copolymer

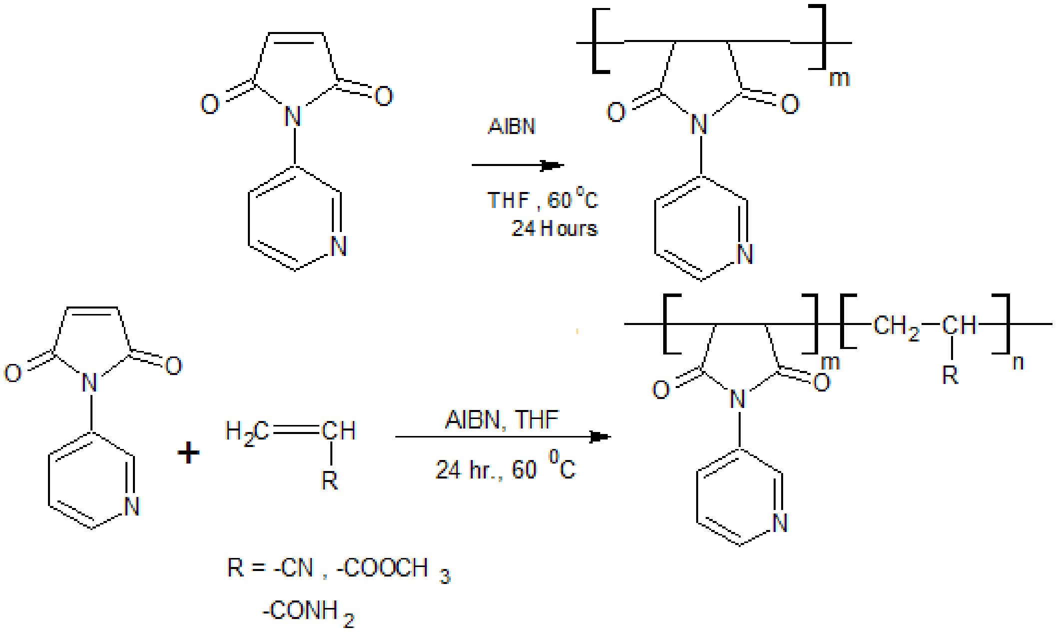
Characterization

Examination of the IR Spectra of monomer [PYMI], homopolymer [H-PYMI] and copolymers PYMI-co- AN, PYMI-co- VA, PYMI-co-AM are reported in the [**Table 2]**. Important chemical shift values of the monomer, homopolymer and copolymers were summarized in **[Table 3]**.

Peaks (cm^{-})					**Characteristics of Peaks**
PYMI	**H-PYMI**	**PYMI-co-AN**	**PYMI -co-VA**	**PYMI -co-AM**	
1715	1716	1715	1716	1715	C=O Sym. &Asym. stretch of imide
1437	1438	1437	1437	1438	C-N-C stretch of N - Substituted maleimide
3088	3099	3098	3096	3094	C-H stretch of aromatic CH=CH
995	**-**	**-**	**-**	**-**	**C-H bending CH=CH**
1542	**-**	**-**	**-**	**-**	**C-C stretch in CH=CH**
1592	1594	1591	1593	1594	C=C stretch in pyridine ring
1471	1472	1470	1468	1473	C=N stretch in pyridine ring
-	-	2978,2929	2977,2927	2980,2928	-CH stretch in –CH_3,-CH_2,
-	-	2241	-	-	-CN
-	-	-	1191	-	--C-O-C stretch of ester
-	-	-	-	3046	-NH

Table 2:FT-IR data of Monomer (PYMI), Homopolymer and copolymers





Scheme 1: Synthesis of PYMI, Homo and Copolymerization

Chemical shift					Characteristics of Peaks
PYMI	**H-PYMI**	**PYMI-co-AN**	**PYMI -co-VA**	**PYMI -co-AM**	
8.4	8.4	8.6	8.3	8.4	Phenyl proton of Ortho to N of imide
8.1 & 7.7	8.1 & 7.7	8.0 & 7.6	8.0 & 7.5	8.0 & 7.6	Phenyl proton of Meta to N of imide
8.5	8.5	8.7	8.7	8.6	Phenyl proton of Para to N of imide
6.8	-	-	-	-	**(-CH=CH-)**
-	3.4	3.6	4.3	3.9	**-CH-CH-**
-	-	1.4	1.3	1.3	**$-CH_2$**
-	-	-	2.9	-	**$-CH_3$**
-	-	-	-	10.3	**-NH**

Table 3:^{1}H-NMR data of Monomer (PYMI), Homopolymer and copolymers

Reactivity Ratio

Monomer reactivity ratios allow prediction of a copolymer composition with starting feed. They are also useful for understanding the kinetics and mechanistic aspects of copolymerization. Elemental analysis has been employed to determine the copolymer composition and to estimate the reactivity ratios of monomer. Here we determine reactivity ratios by Finemann Ross method [7]. The reactivity ratios r_1 and r_2 is the slope of FR plot and its intercept on y-axis, respectively.

Alfrey and price method deals with the resonance stabilization (Q) and polarization characteristics (e) of a monomers and its reactivity behavior with reference to another monomer radical [8].**[Table 4,5]**

Code	Mole Ratio Feed		W% of C-PYMI	Mole Fraction of C-PYMI		Finemann –Ross Method	
	x_1:x_2	% N		Feed $(X)_1$	Copolymer (F_1)	$X_1(1-2F_1)/(1-X_1)F_1$	$X_1^2(F_1-1)/(1-X_1)^2F_1$
C-PYMI-1	1:9	8.51	52.88	0.1	.303	0.1444	-0.0284
C-PYMI-2	2:8	9.11	56.61	0.2	.325	0.2692	-0.1298
C-PYMI-3	3:7	10.92	67.86	0.3	.390	0.2417	-0.2872
C-PYMI-4	4:6	11.46	71.22	0.4	.409	0.2966	-0.6423
C-PYMI-5	5:5	11.73	72.90	0.5	.418	0.3923	-1.3923
C-PYMI-6	6:4	12.17	75.63	0.6	.434	0.4562	-2.9351
C-PYMI-7	7:3	13.43	83.46	0.7	.479	0.2045	-5.921
C-PYMI-8	8:2	14.64	90.98	0.8	.522	-0.3371	-14.7067
C-PYMI-9	9:1	15.51	96.39	0.9	.553	-1.7251	-25.81

Table 4: Parameters for Fineman-Ross Methods to Determine Reactivity Ratios in Copolymers of PYMI with Acrylonitrile (AN)

Polymer Code	Reactivity Ratios(Finemann-Ross Method)		Alfrey and Price Method	
	r_1	r_2	Q	e
C-PYMI	0.0727	0.4122	.87	3.07

Table 5: Reactivity ratios of Monomers

TG analysis

The TG analysis of Homopolymer and copolymers were performed in the temperature range of 20-800℃. At 700℃ the total weight of homopolymers was 12.98%,PYMI-co-AN is 21.594%,PYMI-co-VA is 40.74 ,PYMI-co-AM 20.64 is, corresponding to the release of solvent molecules and 2-aminopyridine. From 500 to 700 ℃, the TG curves of both homopolymer and copolymers exhibit smooth weight losses. It indicates that polymers are stable at temperature lower than 500 ℃.**[Table 6][Figure 1]**

Polymer Code	Weight loss (%)					
	200^0C	300^0C	400^0C	500^0C	600^0C	700^0C
H-PYMI	13.807	35.86	51.492	69.787	92.429	87.014
PYMI-co-AN	11.701	28.955	43.944	54.668	68.677	78.406
PYMI-co-VA	6.470	17.051	34.525	46.379	53.416	59.26
PYMI-co-AM	10.842	24.476	40.942	50.846	70.538	79.357

Table 6: Percentage weight loss of H-PYMI, PYMI-co-AN,PYMI-co-VA,PYMI-co-AM at various temperature range from the TGA.

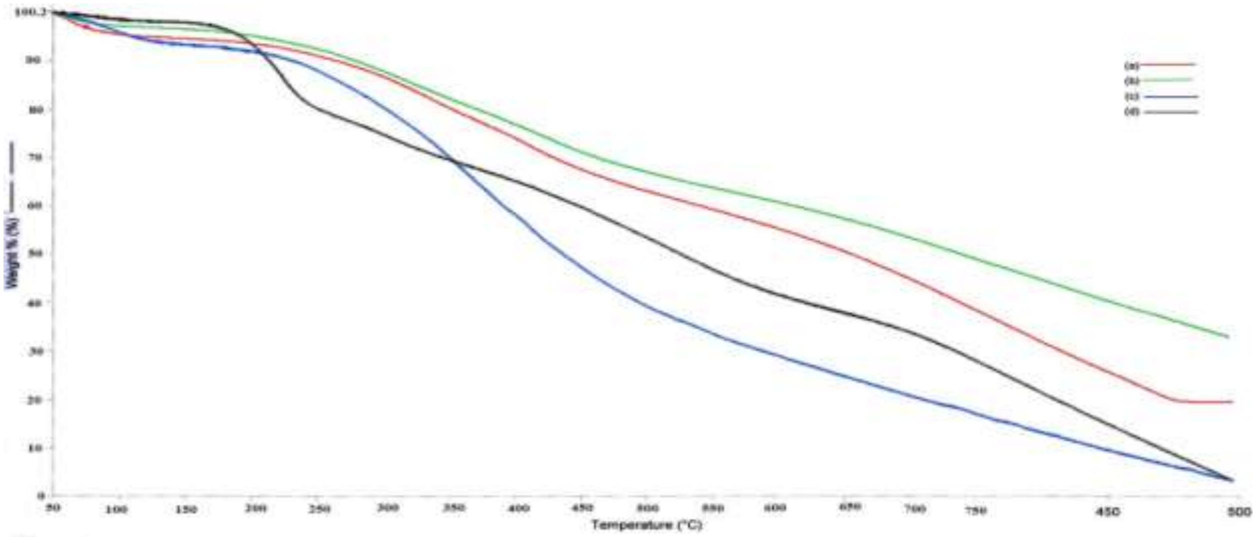


Figure1: TG Analysis (a) H-PYMI (b) PYMI-co-AN (c) PYMI-co-VA (d) PYMI-co-AM

Microbial Activity

Antibacterial and antifungal activities of all newly synthesized compounds were screened by considering zone of inhibition of growth. Copolymers,Homopolymer were screened for their antibacterial activity against *Esherichia coli*, *Staphylococusaureus*and for their antifungal activity against *Aspergillusniger,Alternariasolani*at the concentration of 500µg/mL in THF in the nutrient agar media. The screening tests were performed in triplicate and the results were taken as a mean of three determinations. **[Table 7,8] [Fig. 2,3].**

Code	500(µg/ml) Concentration of compound taken	
	Zone of Inhibition For E. coli(mm)	Zone of inhibition for S. aureus(mm)
H-PYMI	7	9
PYMI-co-AN	8	10
PYMI-co-VA	8	9
PYMI-co-AM	7	11

Table7: Antibacterial activity of H-PYMI and PYMI-co-AN,PYMI-co-VA,PYMI-co-AM against bacteria *Esherichia coli*, *Staphylococusaureus*

Code	100(µg/ml) Concentration of compound taken	
	Zone of Inhibition For A. nizer(mm)	Zone of Inhibition For A. solani(mm)
H-PYMI	**6**	**9**
PYMI-co-AN	**4**	**8**
PYMI-co-VA	**7**	**10**
PYMI-co-AM	**9**	**8**

Table8: Antifungal activity of H-PYMI and PYMI-co-AN,PYMI-co-VA,PYMI-co-AM against fungus *Aspergillusnizer , Alternariasolani*

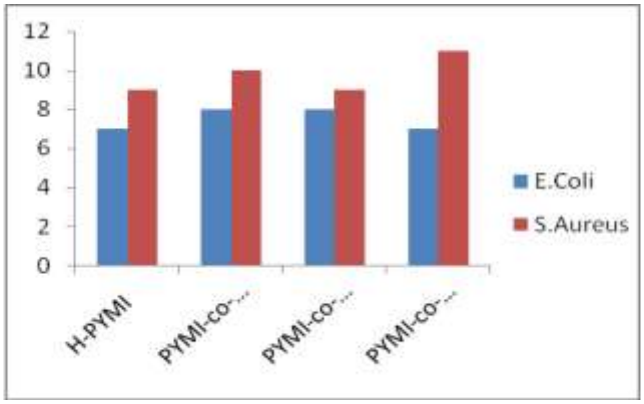


Figure 2: Antibacterial activity of Polymers

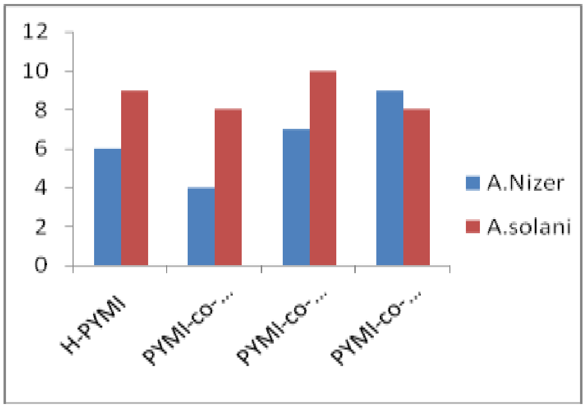


Figure 3. Antifungal activity of Polymers

Conclusion

In present paper we have reported the synthesis of PYMI and its homopolymer and copolymers. The structure of monomer and all polymers were characterized by spectroscopic methods. The synthesized homo and copolymers showed good thermal stability and degraded in one step due to side group elimination. The total heat of combination of the homo and copolymers changes linearly. The change in peak value of heat release rate and char yield depends on the chemical structures of the polymers. The biological activities of polymers were also investigated in this study. These polymers could be promising materials for antimicrobial coating application

Acknowledgement

Authors gratefully acknowledge Head, Department of Polymer Science, M. L. S. University Udaipur for providing lab facility and also SICART, Vallabh Vidhyanagar, Gujarat, SAIF Chandigarh for sample analysis.

References:

[1] C. Hulubei, E.Hamciuc, M. Bruma, and A. Mauller, “Functional Polyimides and Thin Films Based on Them”, Romanian Journal of Information Science and Technology,vol. 11,pp 133-142, 2008.

[2] O.G.Marambio, G. D. C. Pizarro, M.Jeria-Orell, M.Hureta, C.O. Azar and W.D.Habicher, “Poly(N-phenylmaleimide-co-acrylic acid)-Copper(II) and Poly(N-phenylmaleimide-co-acrylic acid)Cobalt (II) Complexes : Synthesis, Characterization, and Thermal behavior”, pp 4933-4940, 2010.

[3] C. E. Brunchi, M. Bercea and S.Morariu, “Hydrodynamic Properties of Polymer Mixtures in Solution”, *J. Chem. Eng. Data*, vol. *55,* pp4399–4405, 2010.

[4] A. Okudan and A. Karasakal, “The Effect of H-Bonding on Radical Copolymerization of Maleic Anhydride with N-tert-Butylacrylamide and Its Characterization”,International Journal of Polymer Science, vol.2013,pp 1-9,2013.

[5] Wisconsin,"Polyacrylamide as a Soil Stabilizer for Erosion Control.", Report No. WI 06-98, January 2001.

[6] J. Chaudhary, S. Purohit, S. Jinger, “ Radical Homo and Copolymerization of Maleimide with Acrylic acid: effect of H-Bonding on Thermal Resistant Properties”,American International Journal of Research in Science, Technology, Engineering & Mathematics, vol. 15, pp 46-54, 2015.

[7] M. Finemann,S.D. Ross, Journal of applied polymer science ,vol. 5,pp 259,1950.

[8] T. Alfrey,C.C. Price, Journal of applied polymer science ,vol. 2 , pp 101, 1947.