IJESRT

INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

COPOLYMERS OF MA/EA/BA WITH N-SUBSTITUTED MALEIMIDE: SYNTHESIS, CHARACTERIZATION AND EFFECT ON THE THERMAL PROPERTIES

Jyoti Chaudhary*, Swati Purohit, Radha Chaudhary
* Department of Polymer Science, M.L.S.U.,Udaipur (Raj.) India
Department of Polymer Science, M.L.S.U.,Udaipur (Raj.) India
Department of Chemistry, GITS, Udaipur (Raj.) India

ABSTRACT

Copolymers of N-[4-(acetylamino) phenyl] maleimide (AAPMI) were synthesized by reacting with Methyl acrylate (MA)/Ethyl acrylate (EA)/Butyl acrylate (BA). All polymers show good solubility in polar solvent. Polymers are structurally characterized by FT-IR and ^{1}H- NMR spectroscopic methods and biologically by antibacterial and antifungal assays for evaluating their potential use for biomedical applications. The compositions of the copolymers as well as reactivity ratios for applied comonomer were determined by Finemann Ross method. Copolymers (C-AAPMI) with various proportions of N-[4-(acetyl)phenyl amino]maleimide (AAPMI) and Butyl acrylate [BA] were prepared by free radical polymerization in tetrahydrofuran (THF) using 2,2'-azo-bis-isobutyronitrile (AIBN) as an initiator at $70 \pm 2°C$. The nine copolymer samples were synthesized from different feed ratio of comonomer. Thermal behavior of homopolymer and copolymers were evaluated by TGA and DSC. Gel permeation chromatography was applied to determine the molecular weights of the polymers.

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

INTRODUCTION

Thermo stable polymeric material with medical application has been considerable interest in the synthesis of copolymers containing maleimide moieties, especially of N-phenyl maleimide. Copolymerization of maleimides with vinyl monomers provides the possibility of synthesizing higher and thermally stable polymers because maleimide compound are the thermal stabilizer. In addition to that the processability of maleimide polymer can also be enhanced by the incorporation of more flexible units within the polymer backbone [1]. Rigid imide ring hinder chair rotation, resulting in greater structural stiffness and higher thermal stability [2].Flexibility was introduce in polymer chain by its copolymerization with vinyl monomer, copolymerization can improve the physical ,mechanical and chemical properties of polymaleimides. In biological applications maleimides are used as chemical probes of protein structure, immuno conjugate for cancer therapy, solid support enzyme for synthetic applications [3]. Maleimide and its derivatives are a kind of very useful monomers. Their corresponding homopolymer or copolymers are widely used as coatings, adhesives, laminations and fibers because of their high heat-resistivity [4].

Herein, we comparises the synthesis and characterization of copolymers containing acrylate-maleimide units as electron rich and electron acceptors units with the results of their thermal and antimicrobial properties. It was observed that such copolymers have better thermal stability than the polymers of vinyl monomers. The studies of physical and spectral properties have been carried out in order to characterize the copolymer sample.

MATERIAL AND METHOD

p-Amino acetanilide and maleic anhydride were recrystallized from acetone and all other chemicals like THF,DMF,AIBN for this work were of analytical grade and used without any purification.

Measurement
FT-IR and ^{1}H-NMR spectroscopy is used to structural characterization of the copolymer. FT-IR spectra were measured on a Shimadhzu – 8201 FT-IR Spectrometer by using KBr pallet technique and ^{1}H-NMR spectra were recorded on   Bruker Avances II 400 NMR Spectrometer. TMS is used as a internal reference. The viscosity measurement of samples were obtain in DMF at 30 ± 0.2 [0]C, using an Ubbelohde suspended level viscometer. Thermal behavior of polymer was measured by TGA and DSC, at a heating rate of 10^0 C/min from 0 [0]C to 650[0]C. Molecular weight was measured by gel permeation chromatography (GPC).

Synthesis
Synthesis of AAPMI (N-[4-(acetylamino) phenyl] maleimide was prepared by the previously describe method [5] involving the reaction of 4-amino acetanilide with maleic anhydride followed by dehydrogenation of the intermediate maleamic acid promoted by an acid catalyst. Monomer was copolymerized with Methyl acrylate (MA)/Ethyl acrylate (EA)/Butyl acrylate (BA).**Scheme 1**

RESULT AND DISCUSSION
Table 1 summarizes the density, viscosity, Number average and weight average molecular weights (Mn, Mw) and polydispersity indexes (Mw/Mn) of synthesized monomer and polymers. Molecular weights (Mn, Mw) and polydispersity indexes (Mw/Mn) of polymers were measured by GPC.

Characterization
The IR spectra of the monomer and polymers shows the characteristic bands, at 1708-1710 and 1777-1779 attributed to the C=O sym. and Asym. Stretch of imide ring , at 1404-1407 cm[-] attributed to the C-N-C stretch of N - Substituted maleimide, C=O stretch of acetyl group at 1677-1685 cm[-],-NH stretch at 3314-3334 cm[-] C-H. C-C stretch in CH=CH are disappear in homo and copolymers at 995 and 1542 cm[-] , which shows that polymerization is takes place by this bond.
Important chemical shift values of the monomer, homopolymer and copolymers at 6.8-7.5ppm due to phenyl proton of ortho and meta to N of imide, at 2.2-2.3 ppm due to –COCH$_3$, at 3.40-3.51 ppm due to –NH. In addition to above all observed signal in the region 6.8-7.74 ppm due to aromatic ring was also found. -CH=CH- chemical shift is disappear and show chemical shift at 3.3-3.4 ppm due to –[CH-CH]$_n$- in homo and copolymers. The FT-IR and ^{1}H-NMR observation support the disappearing the band of –CH=CH- , it shows that polymerization proceed via an opening of the double bond.

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

Polymer Code	ρ(g/cm^3)	η(dl/g)	M_W	M_n	PDI (Poly Dispersity Index)
H-AAPMI	0.4766	0.2745	2560	5880	2.2968
AAPMI-co-MA	0.5185	0.2841	1485	1183	1.2552
AAPMI-co-EA	0.4017	0.2978	1659	1309	1.2673
AAPMI-co-BA	0.5599	0.4798	1845	1347	1.3697
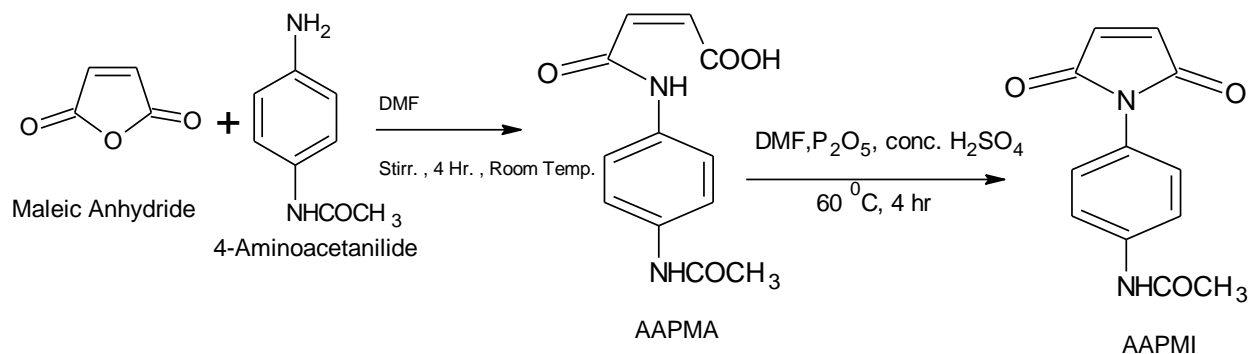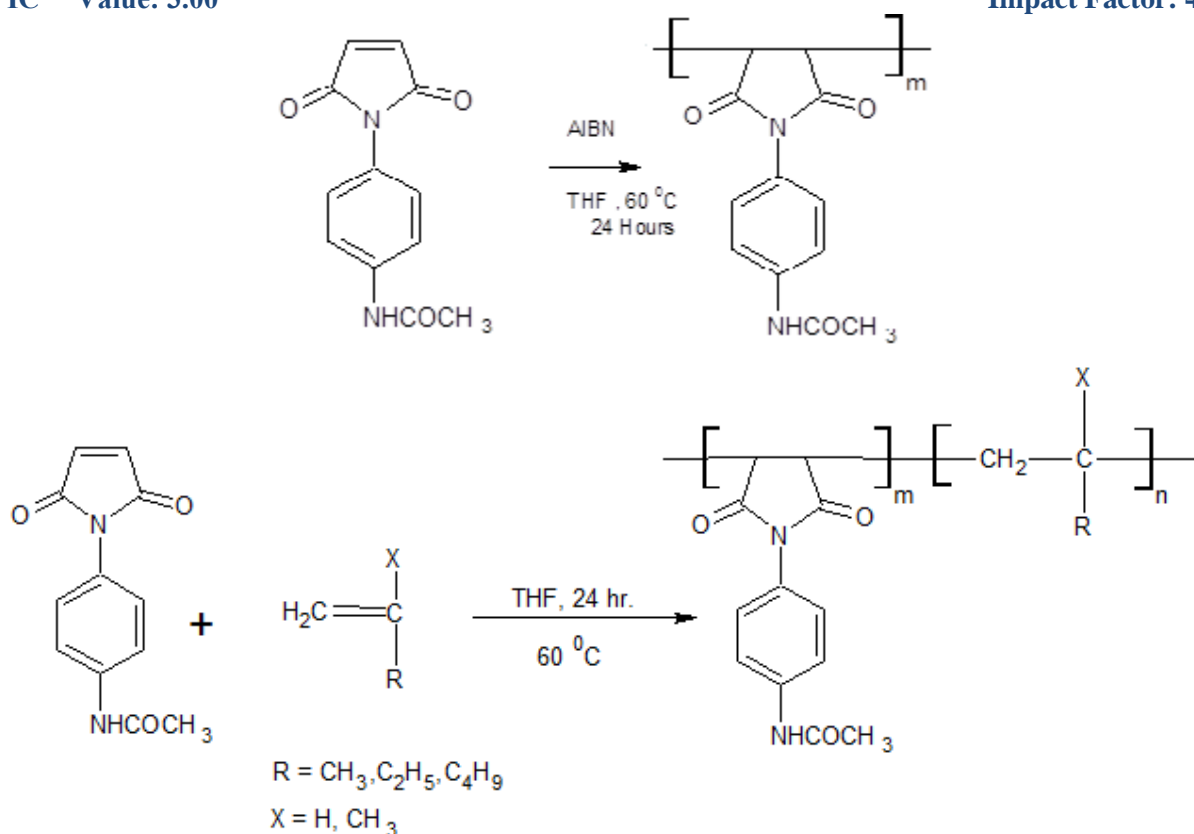
Scheme 1 Synthesis of monomer (AAPMI), Homo and copolymers

Reactivity ratios
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 [6]. The reactivity ratios r_1 and r_2 is the slope of FR plot and its intercept on y-axis, respectively. In our case, the monomer AA is more active over the monomer AAPMI.
The Q, e values which represent the resonance stabilization and polarity of monomers are derived by using Price-Alfrey equation [7]. **[Table 2,3]**

Table 2- Parameters for Fineman-Ross Methods to Determine Reactivity Ratios in Copolymers of AAPMI with Butyl acrylate (BA)

Code	Mole Ratio Feed		W% of C-AAPMI	Mole Fraction of C- AAPMI		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-AAPMI-1	1:9	3.45	28.91	0.1	0.1256	0.666	-0.0859
C-AAPMI-2	2:8	4.96	41.57	0.2	0.1807	0.883	-0.2834
C-AAPMI-3	3:7	5.78	48.44	0.3	0.2106	1.177	-0.6890
C-AAPMI-4	4:6	7.47	62.61	0.4	0.2722	1.11	-1.1894
C-AAPMI-5	5:5	7.68	64.37	0.5	0.2886	1.46	-2.4667
C-AAPMI-6	6:4	7.93	66.47	0.6	0.3021	1.965	-5.20017
C-AAPMI-7	7:3	9.12	76.44	0.7	0.3555	1.897	-10.8998
C-AAPMI-8	8:2	10.05	84.24	0.8	0.4109	1.735	-22.9892

C-AAPMI-9	9:1	10.45	87.59	0.9	0.4734	1.01	-25.4321

Table 3- Reactivity ratios of Monomers

Polymer Code	Reactivity Ratios(Finemann-Ross Method)		Alfrey and Price Method	
	r_1	r_2	Q	e
C- AAPMI	0.0114	1.1895	0.6871	3.1350

Thermal properties

The TG analysis of homopolymer and copolymers were performed in the temperature range of 20-800℃.The decomposition behavior of polymers is shown in Figure 1. At 700℃ the total weight of homopolymers was 34.503 %, AAPMI -co-MA is 31.048%, AAPMI -co-EA is 28.482 %, and AAPMI- co-BA is 26.72%, corresponding to the release of solvent molecules and moisture. 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 ℃.

Based on these results, it is concluded that the acrylate moieties in the copolymers causes some thermal stability, and by increasing the amount of different acrylate moieties and its molar proportion thermal stability is affected. AAPMI-MA has shown maximum thermal stability as compare to AAPMI -EA and AAPMI -BA at 200 ºC. The highest thermal stability of AAPMI -MA among all copolymers is probably due to less bulky pendent groups. **[Table 4][Fig. 1]**

Table 4- Percentage weight loss of Polymers by TGA

Polymer Code	Weight loss (%)					
	200^0C	300^0C	400^0C	500^0C	600^0C	700^0C
H- AAPMI	4.063	11.719	42.812	53.61	60.191	65.497
AAPMI -co-MA	3.498	6.489	38.429	46.591	48.591	68.952
AAPMI-co-EA	5.284	8.942	39.482	49.572	53.943	71.518
AAPMI –co-BA	2.151	10.579	53.03	65.76	71.438	73.28

Antibacterial activity

Antibacterial and antifungal activities of all newly synthesized compounds were screened by considering zone of inhibition of growth. Polymers were screened for their antibacterial activity against *Esherichia coli, Pseudomonas aerogenosa* and for their antifungal activity against *Aspergillus niger, Alternaria solani* at the concentration of 500μg/mL and 100 μg/mL in THF and acetone in the nutrient agar media. The screening tests were performed in triplicate and the results were taken as a mean three determinations. **[Table 5]**
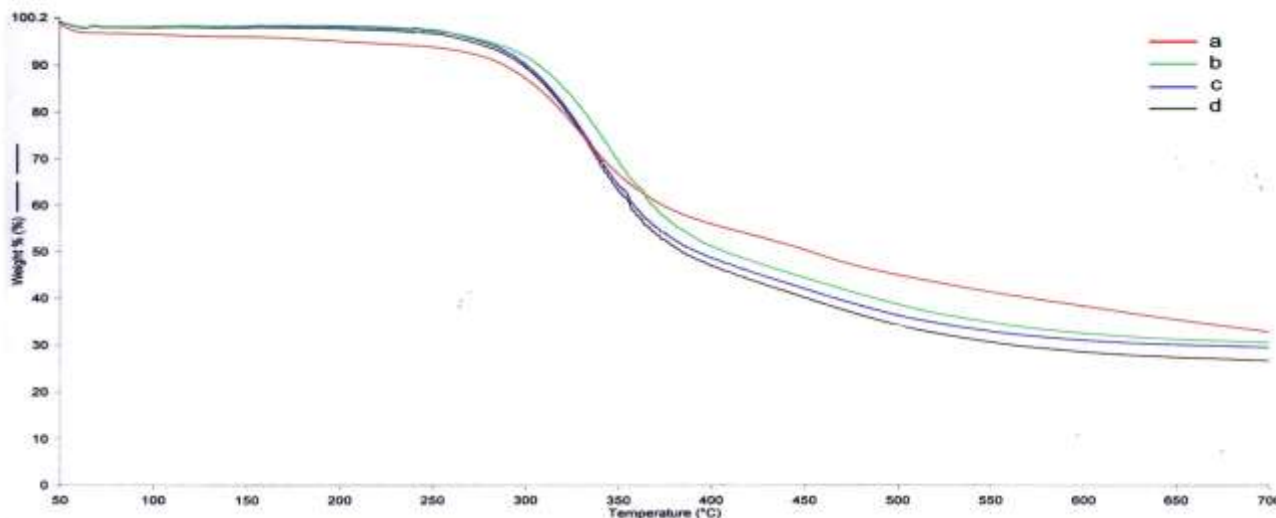

Fig. 1 TG Analysis (a) H-AAPMI (b) AAPMI-co-MA (c) AAPMI-co-EA (d) AAPMI-co-BA

Table 5- Antibacterial and Antifungal activity of Polymers

Code	Zone of Inhibition (mm)			
	Antibacterial activity		Antifungal activity	
	E. coli	P.aerogenosa	A. nizer	A. solani
H- AAPMI	14	8	6	5
AAPMI-co-MA	15	6	9	8
AAPMI -co-EA	15	7	9	8
AAPMI -co-BA	15	9	9	9

CONCLUSION

This work focused on the development of polymers containing thermal with biomedical application. N-Phenyl maleimide and Acrylates were chosen as comonomer. Because of the prevented rotation around C-C bonds in five membered ring structure of maleimides, their polymerization give to a rigid polymer chain and high Tg values. The synthesized homo and copolymers showed good thermal stability and degraded in two step due to side group elimination. The total heat of combination of the homo and copolymers changes linearly. Based on the thermal behavior of the polymer, is predicted that thermal stability of polymers increases as the chain length of the pendent group decreases, due to introduction of flexibility by acrylate monomer. The biological activities of polymers were also investigated in this study. These polymers could be promising materials for antimicrobial coating application.

REFERENCES

[1] L. Yang, L. Zhang, G. Liu, J. Gao, S. Yang and R. Jin, "Synthesis & thermoanalysis of emulsion terpolymers of N-phenylmaleimide, Styrene and acrylonitrile," in Journal of applied polymer science, Vol. 75, pp 1067-1073, 2001.

[2] B.L. Hiran, S N Paliwal, "Synthesis and Free Radical Copolymerization of N-[4-N´-(Benzyl aminocarbonyl)phenyl] Maleimide with Methyl Methacrylate," in Malaysian Polymer Journal (MPJ), Vol. 3, pp 1-12, 2008.

[3] N. P. Shetgiri and B. K. Nayak, "Succinimide synthesis, reaction and biologically activity," in Indian journal of Chemistry, Vol. 44, pp 1933-36, 2005.

[4] W. Decheng, H. Zhaohua and Huang Junlian, "An alternating copolymer of maleimide and atropic acid with narrow molecular weight distribution prepared by radical mechanism," in Science in China, Vol. 4, pp 42,1999.

[5] J. Chaudhary, S. Purohit and S. Jinger, " Radical Homo and Copolymerization of Maleimide with Acrylic acid: effect of H-Bonding on Thermal Resistant Properties" in AIJRSTEM, Vol. 15-315,pp 46-54,2015.

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

[7] T. Alfrey, C.C. Price, Journal of applied polymer science, Vol. 2 , pp101, 1947.