Studies on Heat Resistant Metal Composite of *N*-Substituted Maleimide

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Abstract: *N*-(4-acetylphenyl)maleimide (APMI) was homopolymerized and copolymerized with acrylic acid (AA) at 60-70 $^{\circ}$C in tetrahydrofuran (THF) solution with azoisobutyronitrile (AIBN) as an initiator. Metal composites were also synthesized with various metal such as, Fe^{+2}, Co^{+2}, Ni^{+2} Cu^{+2}. The structure of monomer, homopolymer and copolymer, metal composites were elucidated by FT-IR, ^{1}H-NMR and elemental analysis. The nine copolymer samples were synthesized from different feed ratio of comonomer. The monomer reactivity ratio r_{NAPMI} and r_{AA} were determined by Finemann Ross method. The investigated homo and copolymers showed solubility in polar solvents. Thermal behavior of homopolymer and copolymer were evaluated by TGA and DSC.The molecular weights were determined by GPC. The antimicrobial activity of synthesized homopolymer, copolymer and were screen against various bacteria and fungi and they showed excellent antimicrobial activity.

Keywords: THF, Reactivity ratio, TGA, Finemann-ross method, Antimicrobial activity

Introduction

In recent years studies on polymers, which bind metal ions, have been of great practical interest. The complexing ability of polymers is used in nuclear chemistry, electrochemistry, hydrometallurgy and environmental protection[1]. Maleimide are bio-active compound and used as important building blocks in material science[2].

Incorporation of transition metals into polymer chains offers a possibility to access new useful heat-resistant polymers. Carbonyl group containing maleimide have been reported as metal complexing agent that can form a variety of complexes with various transition and inner transition metal. Some ligand form polymers by complexing with metals and are useful as selective for gas chromatography and they are used as a catalysts, antifriction materials, biologically active substances, electrically conductive coating *etc*.[3]. Water-soluble polymers (WSP) are commercially available and the most important requirements for their use in technological applications are high solubility in water, easy and inexpensive synthesis, an adequate molecular weight and molecular weight distribution, chemical stability, a high affinity for one or more metal ions, and selectivity for the metal ion of interest[4].

N-carbonyl-maleimide copolymers are able to bind metal ions and have been used in waste water purification system as ion-exchange resins, as adhesion promoters for polymer metal film and in the construction of multilayers assemblies[5]. It has been found that the metal-containing polymers possess higher strength and thermal stability and which can be used for industrial production of one-plate glass-reinforced plastic springs for large-loaded motor vehicles[6].

In this paper we focus on the synthesis of series of metal complexes of *N*-substituted maleimide and transition metal to improve the thermal stability of the polymer by incorporation of metal.

Experimental

The following reagents 4-aminoacetophenone, THF, DMF, AIBN, acrylic acid were purchased from Loba chemicals. All chemicals used without further purification. H-APMI was synthesized from maleic anhydride and 4-aminoacetophenone according to the reported methods[7]. The synthesis process of *N*-substituted maleimides is shown in the followingreaction Scheme 1.
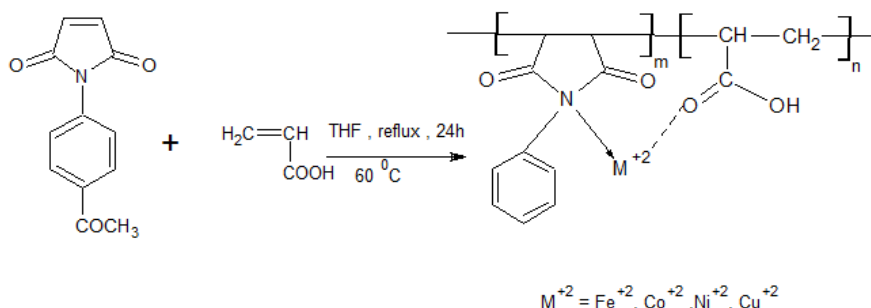
Synthesis of metal complexes

The aqueous solution of 0.01 mole of metal salts was added with constant stirring to an 0.01 mole *N*-substituted maleimide derivative. The reaction mixture was stirred at room temperature for 5 hours. The colored precipitate was obtained (Scheme 2). The precipitate was filtered and washed with water and dried in desiccator.
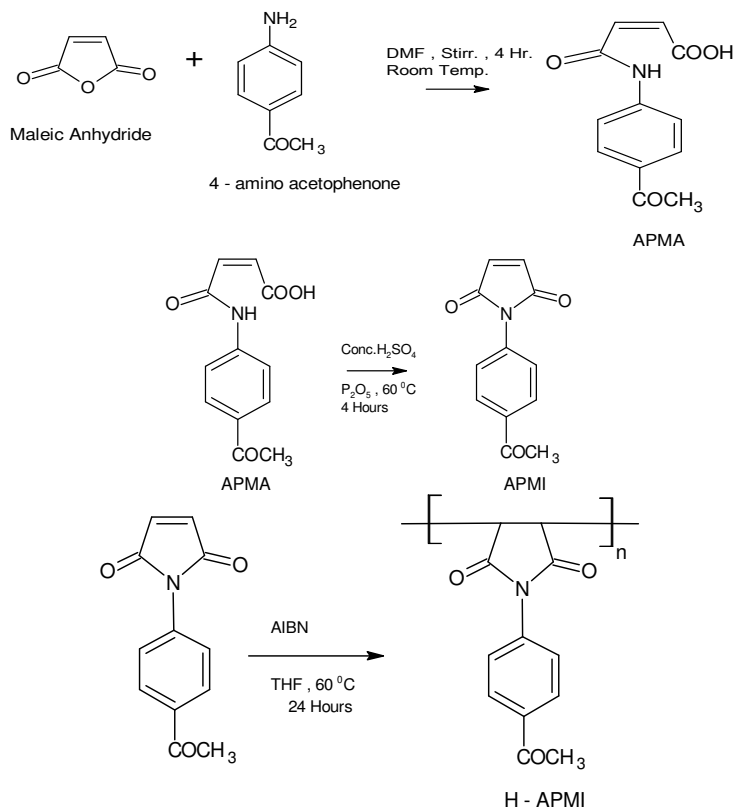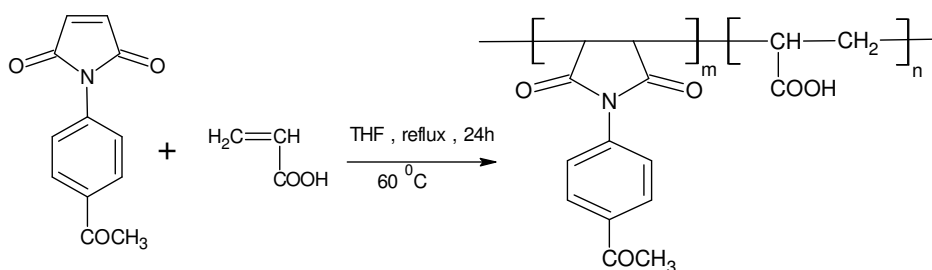
Scheme 1. Synthesis of monomer, homopolymer and copolymer

Scheme 2. Synthesis of metal composites

Results and Discussion

Characterization

Formation of monomer, homopolymer, copolymer and metal complexes was confirmed by FT-IR, ^{1}H NMR and UV-Visible spectra. Fourier transform infrared (FT-IR) spectra was recorded on a FT-IR Perkin-Elmer spectrophotometer model RX-I. The sample was prepared in KBr pellets and the spectrum was obtained in the range 250-4000 cm^{-1}. Nuclear Magnetic Resonance (NMR) spectra of newly synthesized monomer, homopolymer and copolymer have been scanned on BRUKER AVANCE II 400 MHz NMR Spectrometer. TMS was used as a reference.

Structure of monomer (APMI), homopolymer (H-APMI) and copolymer (C-APMI) were evaluated by FT-IR and ^{1}H NMR spectroscopy. IR and ^{1}H NMR spectra of monomer and polymer were shown in Table 1. The peak of (-CH=CH-) was disappear in homopolymer and copolymer showed that polymerization was carried out through this bond.

Analysis of metal complexes

All the metal complexes are colored and non-hydroscopic solid. The formations of metal complexes were emphasized by FT-IR spectra of the complexes. A new band appears at about 1570 cm^{-1} assigned to a carboxylate group formed as a result of reaction occurrences in all complexes. No change occurs in broad band at 3000-3130 cm^{-1} for all complexes, it is due to the no interaction of the hydroxyl group in the complexes with metal ions. The >C=O band of the carboxylic group at 1693 cm^{-1} decreased in intensity for those complexes due to interaction between the carbonyl group and the metal ions. Metal ion was bound to the electron donating N atom from the imide ring, So intensity of N-C stretching at 1404 cm^{-1} is decreases.

The band at 3200-3600 cm^{-1} region can be attributed to the presence of water molecules in all complexes, either as a lattice or in the coordination sphere. Magnetic moments of metal complexes are given in Table 2.

Table 1. FT-IR and ^{1}H NMR spectral data of APMI, H-APMI and C-APMI

Techniques	APMI	H-APMI	C-APMI	Characteristics
FT-IR (cm^{-1})	1780,1716	1175,1716	1172,1714	C=O Sym. &Asym. stretch of imide
	1404	1407	1403	C-N-C stretch of *N* - Substituted maleimide
	3015	3000	3014	C-H stretch of aromatic CH=CH
	1677	1681	1677	C=O Stretch of acetyl group
	2880	2855	2890	-CH$_3$
	1508	-	-	C-C stretch of CH=CH
	976	-	-	C-H bending CH=CH
^{1}H-NMR (ppm)	7.8	6.9	7.7	Phenyl proton of Ortho to N of imide
	7.5	7.6	7.9	Phenyl proton of Meta to N of imide
	2.7	2.7	2.5	-COCH$_3$
	-	-	2.1	-CH2-
	-	-	10.81	-COOH
	-	3.4	4.1	-[CH-CH]$_n$-
	6.4	-	-	(CH=CH)

Table 2. Electronic spectra and magnetic moment of metal complexes

Metal complexes	μ_{eff}	Electronic spectral data , cm^{-1}	Transition
-Fe^{+2}	3.56	12147	$^5T_{2g} \rightarrow {}^5E_g$
-Co^{+2}	4.12	21011	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
		18075	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
		11302	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
-Ni^{+2}	2.3	22011	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
		15034	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
		8123	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
-Cu^{+2}	2.05	22413	C.T.
		15211	$^2E_g \rightarrow {}^2T_{2g}$

Solubility

Synthesized monomer, homopolymer, copolymer soluble in THF, DMF, DMSO, acetone, 1, 4-dioxane, ethyl acetate, chloroform. Whereas insoluble in benzene, toluene, *n*-hexane, dichloromethane. The polymer showed solubility in polar solvents indicates the presence of polar group.

Physical properties

Density (ρ) depends on packing of molecules in the polymer chains. The density of homopolymers and copolymer were determined at 30 °C, by using density bottle. Density of homopolymer and copolymer are given Table 3.

Viscosity measurements on APMI in DMF were carried out at different concentrations ranging from 1.00 to 0.1% of copolymer in DMF at 30 °C using an Ubbelohde viscometer with a capillary diameter of 0.49 mm. Measurements of each concentration were repeated three or four times Table 3.

Molecular weights of the synthesized polymer were determined by GPC using GPC-HLPC, molecular weight of homopolymer and copolymers were analyzed on a Turbo matrix – 40 Perkin Elmer, in THF solvent. Molecular weight and polydispersity index of Homo and Copolymer were determined by GPC using THF as a solvent. The number average molecular weight (M_n), weight average molecular weight (M_w) and Polydisperity (M_w/M_n) are furnished in Table 3.

Table 3. Density, Intrinsic viscosity, Molecular Weight of Homopolymer and Copolymer

Polymer Code	$\rho(g/cm^3)$	$\eta(dl/g)$	M_n	M_w	PDI (Poly dispersity index)
H-APMI	0.379	0.2203	114.2	150.2	1.3154
C-APMI	0.5805	0.231	100.7	144.7	1.4378

Copolymer composition and reactivity ratios

The copolymer compositions were determined by elemental analysis (content of nitrogen). Table 4 & 5. From the monomer feed ratios and the resultant copolymer compositions, the reactivity ratios of APMI and AA were evaluated by the Fineman-Ross method(FR)[8]. The reactivity ratios r_1 and r_2 is the slope of FR plot and its intercept on y-axis, respectively.

Alfrey and price derived a relationship to compute the reactivity ratios of various monomers. This method deals with the resonance stabilization (Q) and polarization characteristics (e) of a monomers and its reactivity behavior with reference to another monomer radical[9].

Table 4. Parameters for Fineman-Ross methods to determine reactivity Ratios in copolymer of C-APMI

Code	Mole ratio feed		W% of C-APMI	Mole fraction of C-APMI		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-APMI-1	1:9	3.12	47.92	0.1	.228	0.2782	-0.0432
C-APMI-2	2:8	3.76	57.75	0.2	.368	0.1793	-0.1070
C-APMI-3	3:7	4.02	61.75	0.3	.487	0.0228	-0.1932
C-APMI-4	4:6	4.32	66.35	0.4	.508	-0.0209	-0.4305
C-APMI-5	5:5	5.22	80.18	0.5	.672	-0.5119	-0.4880
C-APMI-6	6:4	5.43	83.41	0.6	.713	-0.8968	-0.9061
C-APMI-7	7:3	5.79	88.94	0.7	.783	-1.6931	-1.5099
C-APMI-8	8:2	6.09	93.54	0.8	.835	-3.2095	-3.1616
C-APMI-9	9:1	6.19	95.08	0.9	.842	-18.3285	-8.2261

Table 5. Reactivity ratios of polymer

Polymer Code	Reactivity ratios (Finemann-Ross method)		Alfrey and Price method	
	r_1	r_2	Q	e
C-APMI	0.434	0.507	0.446	2.00

Effect of solvent – initiator

The effect of different solvents and initiator on percentage yield of homo and copolymers was examined. It was observed that percentage yield in THF-AIBN system is high as compared to DMF, Acetone, Dioxane solvents. So the THF-AIBN was the best choice for this reaction Table 6.

Table 5. Effect of solvents and initiators on percentage yield of polymer

Solvents	Solvent viscosity	Polymerization Time	% Yield in AIBN initiators H-APMI	% Yield in BPO initiators H-APMI	% Yield in AIBN initiators C-APMI	% Yield in BPO initiators C-APMI
DMF	1.299	18 h	30.94	27.18	33.85	32.45
Acetone	1.359	18 h	28.08	27.78	31.42	32.05
Dioxane	1.416	18 h	33.15	30.25	44.52	45.52
THF	1.497	18 h	41.59	39.87	51.16	46.81

Thermal behavior

TGA analyses for polymers were conducted on a PerkinElmer Pyris1 TGA, Temperature Range of TGA: Room Temperature to 1000 ºC, with a heating rate of 10 °C/min in nitrogen. TGA measures the weight change in materials as a function of time and temperature. The thermal stability of APMI was evaluated from their TG curves. Copolymers showed a one-step mass loss process with a slow decomposition process in the range of 200-700 ℃. Thermal stability of the metal composites decreases with the decrease in electronegativity of metal. TGA data shows that thermal stability of metal composites is higher thanthe normal polymer, because thermal stability of polymer increase as the internal rotation hindered and rigidity increases. By formation of composites rigidity increases because due to cross linking in metal and ligand group of polymer a small chelate ring is formed. In Metal composites of Ni^{+2} at 700 ^{o}C, 43.86% weight is remaining and highest thermal stability and Cu^{+2} at 700 ^{o}C, 39.96% weight is left and show lowest thermal stability. Stability order of composites are $Ni^{+2} > Fe^{+2} > Co^{+2} > Cu^{+2}$. The TGA results are summarized in Table 6.

Table 6. Percentage weight loss of H-APMI, C-APMI, C-APMI-M^{+2} at various temperature range from the TGA

Polymer code	Weight loss, %					
	200 ^{o}C	300 ^{o}C	400 ^{o}C	500 ^{o}C	600 ^{o}C	700 ^{o}C
H-APMI	10.01	17.21	20.29	31.68	43.94	59.56
C-APMI	19.52	26.42	36.34	48.91	57.42	61.34
C-APMi-Fe^{+2}	8.84	25.78	37.21	45.86	58.43	32.04
C-APMi-Co^{+2}	10.83	24.84	36.57	47.99	50.12	58.47
C-APMi-Ni^{+2}	6.92	24.39	33.89	42.87	46.14	56.14
C-APMi-Cu^{+2}	12.14	24.894	42.13	43.84	55.14	60.04

Microbial activity

Antibacterial and antifungal activity of all newly synthesized compounds was screened by considering zone of inhibition of growth. Copolymer, homopolymer at the concentration of 50 μg/mL in methanol in the nutrient agar media were screened for their antibacterial activity against *Esherichiaaerogenes, Staphylococusaureus* and for their antifungal activity against *Aspergillusniger, Alternariasolani*. The screening tests were performed in triplicate and the results were taken as a mean of three determinations (Table 7, 8).

Table 7. Antibacterial activity of APMI, H-APMI and C-APMI against bacteria *Esherichiaaerogenes, Staphylococusaureus*

Code	500, μg/mL Concentration of compound taken	
	Zone of inhibition for *E. aerogenes,* mm	Zone of inhibition for *S. aureus,* mm
APMI	6	7
H-APMI	8	7
C-APMI	9	10

Table 8. Antifungal activity of APMI, H-APMI, C-APMI against fungus *Aspergillusnizer, Alternariasolani*

Code	100, μg/mL Concentration of compound taken	
	Zone of inhibition for *A. nizer,* mm	Zone of inhibition for *A. solani,* mm
APMI	5	5
H-APMI	6	4
C-APMI	8	10

Conclusion

Synthesis of metal complex of copolymer of *N*-[4-(acetyl) phenyl] maleimide (APMI) with acrylic acid has been reported. Acrylic acid were used as ligands for transition metals. FT-IR analysis showed formation of carboxylate formation in the cross-linked copolymer. Metal composites of Fe^{+2}, Ni^{+2} Co^{+2} and Cu^{+2} were partially soluble or insoluble in common organic solvents. The thermal stabilities of the complexes decreased with the decrease of metal electronegativity. Fe(II) complex show good electrochemical and thermalystabal propertiesand exists a tremendous interest in use of conducting polymers in electronics applications. All synthesized homo and copolymer showed good antimicrobial activity, could be ideal candidates for antimicrobial coating application.

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