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Synthesis, characterization and biological screening of cobalt containing polymer films

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Cobalt containing copolymer films have been synthesized by copolymerisation of methyl methacrylate and acrylonitrile containing different concentrations of poly cobalt methacrylate. The copolymerisation was initiated by cadmium complex of Schiff base. The synthesized copolymer films have been characterized by ^{1}H NMR, IR and elemental analysis. Other properties such as thermal and chemical resistance, electrical conductance, adsorbity, permeability, softening range, molecular weight and biocidal effect have been studied.

Keywords: Methyl methacrylate, acrylonitrile, poly cobalt methacrylate, molecular weight, thermal analysis, biological screening

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Polymer chemistry has emerged as an active discipline of modern science in the world. During the past 50 years polymers had a marked and direct practical impact on the way of life of people in nearly every region of the world. Day-by-day metal containing polymers are becoming increasingly important[1-4] and have found extensive application in the field of engineering[5]. They have also found application as light adhesives, sensitive media for photocopying devices, combustion moderators, flame extinguishers and electrically conducting meterials[6-10]. Many metal containing polymers have antimicrobial properties[11]. Metal containing polymers based on lead and tungsten metallocene monomers have been used as coating for target in laser induced thermonuclear synthesis[12].

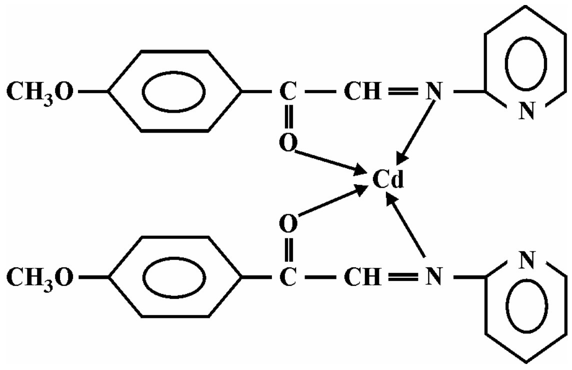
During the past decades synthesis of polymer films has revolutionised research in the field of polymer chemistry[13]. In the present article is presented the preparation of new types of polymer films of methyl methacrylate and acrylonitrile containing poly cobalt methacrylate.

Materials and Methods

Commercial grade methyl methacrylate (MMA) and acrylonitrile (ACN) were purified according to Overberger's method[14]. α,α'-Azobisisobutyronitrile (AIBN) was purified by recrystallization from ethanol. Cobalt methacrylate has been prepared by the same method as reported in literature[15]. Poly cobalt methacrylate has been prepared by using AIBN as an initiator at 85ºC. Copolymer samples of methyl methacrylate with acrylonitrile of different weight ratios have been prepared by using cadium complex of 2-(*p*-methoxyphenylcarbonylazomethine)pyridine as an initiator. The initiator has been prepared *via* the following two steps:

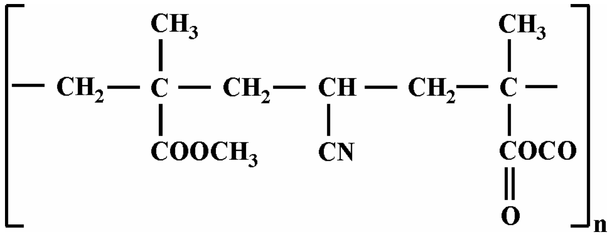
(i) **Preparation of 2-(*p*-methoxyphenylcarbonylazomethine) pyridine (MPCAP)**: 1.6 g of *p*-methoxyphenyl glyoxal was mixed with 0.9 g of ethanolic solution of 2-aminopyridine. The mixture was refluxed for 4 h. Dark brown crystals were obtained which were purified by recrystallization and dried in vacuum. m.p. > 200ºC; IR (KBr or nujoll or $CHCl_3$ *etc*): 1700 (C=O), 1600 cm^{-1}(C=N). Anal. $C_{14}H_{12}O_2N_2$ requires C, 56.75; H, 4.41; N, 8.76. Found C, 57.20; H, 4.94; N, 9.26%.

(ii) **Preparation of dichloro[2-(*p*-methoxyphenylcarbonylazomethine) pyridine] cadmium (II) (MPCAP-Cd)**: The ethanolic solution of 1.0 g of cadmium chloride was mixed with 1.2 g of MPCAP and refluxed for 4 h at 80ºC. The resultant solid was washed and finally refluxed with ethanol and dried in vacuum over anhydrous calcium chloride. Description: Pink coloured amorphous solid m.p. 124ºC; IR (KBr or nujoll or $CHCl_3$ *etc.* 1680 (C=O), 1620(C=N), 500(Cd-N), 320 cm^{-1} (Cd-Cl). Anal. $[Cd(C_{28}H_{24}O_4N_4)Cl_2]Cl$ requires C, 39.68; H, 2.85; N, 6.61. Found C, 40.06; H, 2.97; N, 6.49%.



Preparation of film solution: Films were grown by dissolving the copolymer of methyl methacrylate and acrylonitrile in benzene using a fixed concentration of 15% by weight of the solute. The solution was continuously stirred for about 1 h using a magnetic stirrer to ensure homogenous mixing. For preparing metal containing polymer films, different concentration (25, 50 and 100 mg) of poly cobalt methacrylate were also added (**Table I**).

Copolymers of methyl methacrylate and acrylonitrile have been prepared by polymerising the monomers using dichloro[2-(*p*-methoxyphenylcarbonyl-azomethine)pyridine] cadmium (II) as an initiator in different weight ratios by varying the concentration (1:1, 1:2, 1:3, 2:1, 3:1) of monomers at 80ºC.



$$\left[-CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-CH_2-\underset{CN}{CH}-CH_2-\underset{\substack{COCO\\ \|\\ O}}{\overset{CH_3}{C}}- \right]_n$$

Preparation of films: The films were prepared by pouring the film solutions on clean dry glass plates. The glass plates were tilted back and forth to spread the solution uniformly after which they were kept at 20ºC in an oven for drying.

Molecular weight: Molecular weight was determined by gel permeation chromatography using styragel columns and polystyrene standards. Toluene was used as the mobile phase with a flow rate of 1.0mL/min.

Table I — Composition of reactant used in the preparation of cobalt containing polymer films

Polymer film code	Components		MPCAP-Cd (mg)	Polycobalt methacrylate (mg)
	MMA (M)	ACN (M)		
PF_1	6.11	5.27	6.17	-
PF_2	6.11	5.27	6.17	25
PF_3	6.11	5.27	6.17	50
PF_4	6.11	5.27	6.17	100
PF_5	4.53	7.81	6.19	50
PF_6	3.60	9.35	3.35	50
PF_7	7.39	3.17	5.60	50
PF_8	7.95	2.27	5.35	50

Electrical conductance: The electrical conductance of the polymer films was checked by Toshniwal conductivity meter type CL 01-07A using acetone as the reference solvent.

Thermogravimetric analysis: Thermogravimetric analysis of the films were carried out using Perkin-Elmer thermal analyzer. TG and DTG curves were recorded over the temperature range 25º to 500ºC at constant heating rate of 15º/min. Controlled dynamic atmosphere of nitrogen in air was used in the furnace.

Permeation Experiment: In order to investigate the water permeability through the film, the end of a test tube, containing saturated sugar solution was sealed with the film. The test tube was then placed in a beaker containing a solution of methylene blue dye and this system was left for 24 h.

Solubility and Chemical resistance: Solubility of the films was checked by immersing the film strips (about 50 mg in weight) at 30º and 70ºC. The change in weight was noted.

Adsorption Experiment: In order to study the phenomenon of adsorption, film strips (about 50 mg in weight) were immersed in various solvents (ethanol, diethyl ether and nitric acid) at 60ºC. After a relatively short time the increase in weight due to adsorption was noted.

Biological screening: Biological screening of the films were carried out against two kinds of microorganisms *viz* bacteria and fungi using 'agar disc diffusion method'[16]. The screening was made at 250, 500 and 1000 ppm in acetone and the number of replications in each case was three. *Escherichia coli, Staphylococcus aureus, Aspergillus niger* and *Aspergillus flavus* were used as test organisms for bactericidal and fungicidal activity. Sterilized filter paper discs of 5 mm diameter were soaked in solutions of different concentration of test compounds and introduced into nutrient agar plates. The plates were incubated for 24 h at 37ºC for bacteria and 96 h at 28ºC for fungi. The zones of inhibition based upon zone size around the discs were measured.

Results and Discussion

The films were transluscent, soft and greenish blue in colour. They were found impermeable to water.

Molecular weight: Gel permeation chromatography data of the polymer films show that they are of high molecular weight distribution. The molecular weight of polymer changes with the change in molar ratio of the monomers in the feed. In the polymer systems it is well established that the reactivity of methyl methacrylate is much higher than its comonomer resulting in high methyl methacrylate content of the copolymer but a definite relationship could not be established between the polymer composition and the molecular weight of the polymer films. The polydispersity of different polymer films lies in the range of 2.34-2.73 and intrinsic viscosities varies from 0.204 to 0.252 indicating that these have reasonably good film forming capacities (**Table II**).

Electrical conductance: The conductivity values of all metal containing polymer films at RT were found to be higher and this may be due to the presence of metal in the main side chain of the polymer. Organic polymers are generally insulators because their valence band is full, their conduction band is empty and the two are separated by a large energy gap. Metals conduct electricity because they have partially filled bands. Thus an organic polymer becomes conducting because alloying leads to either the valence or the conduction band ending up being partially filled. Further, a comparative study of the electrical conductance value of polymer films in the absence of metal shows an increase in conductivity value with increasing acrylonitrile content which is due to the greater presence of cyano group (**Table II**).

Table II — Physical properties of cobalt containing polymer films

Polymer Film Code	Molecular weight	Specific Conductance (μmole/ cm)	Softening range ºC
PF_1	1, 37, 864	2.2	118-25
PF_2	-	6.4	125-35
PF_3	1, 60, 942	10.6	117-22
PF_4	1, 69, 989	11.2	108-19
PF_5	-	9.1	105-19
PF_6	-	10.6	110-18
PF_7	-	8.8	114-24
PF_8	-	8.2	117-18

Thermogravimetric analysis: TG and DTG data indicate that the polymer film PF_3 decomposes mainly in two stages, the major portion getting decomposed in the second stage. The initial decomposition temperature increases with the increase in methyl methacrylate content in the polymer system. This may be due to intramolecular hydrogen bonding. The decomposition temperatures were determined by the intersection of the tangent to the steepest portion of the TGA curve with its straight line. The initial temperature for the second stage degradation is also higher when MMA content is higher in the polymer film. The thermostability of metal containing polymer film PF_3 increases when compared with PF_1 which has no metal content. This is due to crosslinking. Crosslinking increases rigidity of the chain thus imparting thermal reinforcement to the polymer.

Solubility and Chemical Resistance: The polymer films display good chemical resistance. They were completely soluble in DMF, dichloroethane, ethyl acetoacetate, ethyl malonate, acetic acid, chloroform, dioxane, benzene and acetone; partially soluble in DMSO and insoluble in other solvents like carbon tetrachloride, toluene, methanol, ethanol, ether, hydrochloric acid, nitric acid, sulphuric acid, sodium hydroxide and water (**Table III**). The solubility

Table III — Solubility of cobalt containing polymer film PF_3

Solvent	Temperature	
	30ºC	70ºC
Dimethyl formamide	+ +	+ +
Dimethyl sulphoxide	+ -	+ -
Dichloroethane	+ +	+ +
Ethyl acetoacetate	+ +	+ +
Ethyl malonate	+ +	+ +
Acetic acid	+ +	+ +
Chloroform	+ +	+ +
Carbon tetrachloride	- -	- -
Dioxane	+ +	+ +
Benzene	+ +	+ +
Toluene	- -	- -
Methanol	- -	
Ethanol	- -	- -
Acetone	+ +	
Diethyl ether	- -	- -
Sulphuric acid	- -	- -
Nitric acid	- -	- -
Hydrochloric acid	- -	- -
Water	- -	- -
Sodium hydroxide	- -	- -

+ + = Completely soluble
- - = Insoluble
+ - = Partially soluble

decreases with passage of time which is due to inter and intramolecular linkages. The ultraviolet radiation from sunlight abstracts hydrogen from the nearby polymer films and leads to crosslinking of the polymer chain[17]. The oxidative degradation usually leads to discolouration, hardening and surface changes which is also a reason for the decrease in the solubility of polymer films.

Adsorption Properties: The adsorption property of polymer films was checked in nitric acid, ethyl alcohol and diethyl ether at 50ºC over a period of 1 h. The adsorption isotherms consist of an initial steep rise in adsorption followed by a plateau region where adsorption is almost constant even with increase in polymer concentration. Since these are poor solvents relative to others, adsorption is higher from a poor solvent. At final saturation adsorption point, the polymer shows the highest adsorption on the adsorbent surface. This is due to the smaller size of methyl group and better accessibility of the acrylonitirle group to the adsorbent surface[18] .

Biological Screening: All the polymer films were tested for their cidal action against *E.coli*, *S. aureus*, *A. niger* and *A. flavus* using 'agar disc diffusion method' at a concentration upto 1000 ppm and compared with polymer film having no metal content. The polymer film PF$_4$ having highest metal content displayed maximum (6.0 mm) activity against *S. aureus* while PF$_3$ having moderate concentration of metal showed appreciable (4.0 mm) activity. The activity displayed by the polymer film PF$_6$ having more acrylonitrile content was also good (5.0 mm) against *S. aureus* and appreciable activity (1.0 mm) against *E. coli*. In case of *A. flavus*, the polymer film PF$_8$ having highest MMA content showed good (4.0 mm) activity. The polymer films were ineffective against *A. niger* species upto 1000 ppm concentration. All other polymer films having variable monomer and metal concentration were physiologically active. However, their biostatic action was specific and selective *vis-a-vis* the nature of applied microbial species. Further, a comparative study of the biocidal character of the polymer films showed an increase in the cidal action with increasing metal content which was due to the lethal nature of the metal for the cells of the microorganisms (**Table IV**).

Table IV — Biological screening data of cobalt containing polymer films
(Inhibition of radial growth in mm)
Bactericidal activity conc in ppm

Polymer film code	*Escherichia coli*			*Staphylococcus aureus*		
	250	500	1000	250	500	1000
PF$_1$	-	-	0.5	-	0.5	1.0
PF$_2$	-	-	0.5	-	1.0	2.0
PF$_3$	-	0.5	0.5	2.0	3.0	4.0
PF$_4$	-	0.5	0.5	4.0	5.0	6.0
PF$_5$	-	0.5	1.0	1.0	3.0	4.0
PF$_6$	0.5	0.5	1.0	1.0	4.0	5.0
PF$_7$	-	-	0.5	-	-	2.0
PF$_8$	-	-	-	-	2.0	3.0

Time = 24 h
Temperature = 37 ± 0.1ºC

Fungicidal activity conc in ppm

Polymer film code	*Aspergillus niger*			*Aspergillus flavus*		
	250	500	1000	250	500	1000
PF$_1$	-	-	-	-	-	-
PF$_2$	-	-	-	-	-	-
PF$_3$	-	-	-	-	-	-
PF$_4$	-	-	-	-	-	-
PF$_5$	-	-	-	-	-	-
PF$_6$	-	-	-	-	-	-
PF$_7$	-	-	-	-	-	-
PF$_8$	-	-	-	-	1.0	4.0

Time = 96 h
Temperature = 28 ± 0.1ºC

Characterisation

(i) **Spectral Studies**: In the ^{1}H NMR spectra, the absence of peaks due to unsaturated protons between δ 4-5 indicates that the copolymers are free from monomer impurities. It is well known that the relative integral intensities of peaks due to comonomers are directly proportional to the copolymer composition. The peaks due to aliphatic protons (*iDi.* methyl, methylene and methine) appear at δ0.1-1.8 The methoxy protons of the ester group resonate at δ3.7.

The FTIR spectrum of the polymer films shows a band at 1730 cm^{-1} for the ester group. The sharp band at 1720 cm^{-1} is due to the carbonyl group of methyl methacrylate comonomers. The absence of monomer impurities in the copolymer samples was confirmed by the absence of the band at 1600 cm^{-1}. The aliphatic C-H stretching vibrations show bands at 3100 and 3010 cm^{-1} for methyl and methylene respectively. It is interesting to note that the intensity of the band at 910 cm^{-1} due to methoxy group decreases proportionately with decrease in methyl methacrylate content in the copolymer. The sharp band at 1780 cm^{-}

^{1} is due to the ester group. The metal oxygen bond shows a band at 620 cm^{-1}. The C-H bending vibration shows bands at 1430, 990 and 910 cm^{-1}. The cyano group gives a sharp peak at 1440 cm^{-1}. The spectral patterns of all the polymer films in the same series closely resemble each other.

(ii) **Elemental analysis**: The percentage of carbon, hydrogen and nitrogen in the polymer film have been found to be 58.09, 6.25 and 3.50% respectively.

Conclusion

On the basis of the various studies, it may be concluded that the films have good electrical conductance, thermal stability and antimicrobial effect. The films were soft, water impermeable and were highly absorptive for nitric acid.

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