Available online at www.derpharmachemica.com

Scholars Research Library

Der Pharma Chemica, 2010, 2(6): 442-449
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X

Synthesis, characterization and biological screening of calcium containing polymer films

Suruchi

Department of chemistry, Hindustan College of Sci. & Tech., Farah, Mathura

---

ABSTRACT

Calcium containing copolymer films have been synthesized by copolymerization of methyl methacrylate.The. and acrylonitrile containing different concentrations of polycalcium methacrylate.The copolymerization was initiated by cadmium complex of Schiff base. The synthesized copolymer films have been characterized by H^1 nmr,ir and elemental analysis. Other properties such as thermal and chemical resistance, electrical conductance, molecular weight and biocidal effect have been studied.

Key words: Methyl methacrylate, acrylonitrile, poly calcium methacrylate,thermal analysis, biological screening

---

INTRODUCTION

There has been much interest in recent years in developing and improved understanding of alloys or metal containing polymer films, although the literature includes very few reports in the synthesis and characterization of polymer films in the conventional method of polymerization, monomers may just add to make addition polymer or to may react to form a condensation polymer[1,2]. The polymerization copolymerization of salts of acrylic methacrylic acid in aqueous solutions and in solid state showed the properties of polymers are generally modified influence of cations on reactivities, reaction rate and molecular weights of products[3,4]. However literature survey reveals very few information in the interaction and compatibility of poly metal acrylate (s) .The use of complexes as initiator in various polymerization reactions have been reported[5,6].

MATERIALS AND METHODS

Commercial grade MMA and ACN were purified according to Overberger's method[7].Calcium methacrylate.The has been prepared by the method reported in literature[8].Poly Calcium methacrylate.The has been prepared by using Benzoyl per oxide as an initiator. Copolymer samples of methyl methacrylates with acrylonitrile of different weight ratios have been prepared by using cadmium complex of 2-p- methoxyphenylcarbonylazomethine)pyridine as an initiator. The initiator has been prepared as follows-

1.1-Preparation of 2-(p-methoxyphenylcarbonylazomethine)pyridine(MPCAP):
1.6 g of p-methoxyphenyl glyoxal was mixed with 0.9g of ethanolic solutions of 2-aminopyridine.The mixture was refluxed for 4h.Dark brown crystals were obtained which were purified by recrystallization and dried in vacuum.
Characterization: m.p.>200^{0}C;ir:1700cm^{-1}(C=O)),100 cm^{-1} (C= Ncm^{-1}),Elemental:calculated-C=56.75;H-4.412;N-8.76found,C-57.20;H4.94;N-9.26%

1.2Preparation of dichloro[2-(p-methoxyphenylcarbonylazomethine)pyridine]cadmium (II) (MPCAP-Cd):
The ethanolic solution of 1.0g of cadmium chloride was mixed with 1.2g of MPCAP and refluxed for 4h at 80^{0}C.The resultant solid was washed and finally refluxed with ethanol and dried in vacuum over anhydrous calcium chloride, a pink colored amorphous solid was obtained . Characterisation:m.p.-124^{0}C;ir-1680 cm^{-1}(C=O)1620 cm^{-1}(C=N),500 cm^{-1}(Cd-N),320 cm^{-1}(Cd-Cl)

Elemental:calculated:C-39.68,H-2.85,N-6.61%; ound:C-40.06,H-2.97,N-6.49%: $[Cd(C_{28}H_{24}O_4N_4)Cl_2]Cl$

1.3-Preparation of Film solution-Copolymers of MMA and CAN have been prepared by polymerizing the monomers using dichloro[2-(p-methoxyphenylcarbonylazomethine)pyridine]-cadmium(II) as an initiator in different weight ratios by varying the concentrations of monomers.Table-1

Table-1: Composition of the reactant used in the synthesis of Polycalcium methacrylate containing polymer film

Polymer film code	MMA (mol$^{-1)}$	AN (mol$^{-1)}$	MPCAP-Cd (mol^{-1}x10^{-3})	Poly calcium methacrylate(mg)
PC1	6.11	3.3	5.24	-
PC2	6.11	3.3	5.24	25
PC3	4.53	9.9	6.24	50
PC4	3.6	2.27	3.35	100
PC5	11.4	7.81	5.6	50
PC6	16.1	3.3	5.35	50

Films were grown by dissolving the copolymer of MMA and CAN in benzene using a fixed concentration of 15% by weight of solute, with continuous stirring. For preparing metal

containing polymer films ,different concentrations of poly calcium methacrylate.The have also been added.Table-1

1.4-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.

Characterization:

Fourier Transform infrared analysis-A thin film of polymer solution (0.5mg/ml) in spectroscopic grade solvent was casted on NaCl cell. For recording the FTIR of the polymers on a Perkin-Elmer 599B spectrophotometer.

Nuclear magnetic resonance spectra-H^1-nmr spectrum was recorded on AC-300F nmr spectrometer using appropriate solvent at ambient temperature. TMS was used as internal standard.

Molecular weight determination-Molecular weight was determined by gel permeation chromatography using styragel columns (10^5, 10^4, 10^3, Å) with polystyrene standards. Toluene was used as mobile phase with flow rate of 1.0 ml/minute.

Thermogravimetry-Thermal stabilities of polymer alloy films were carried out on Perkin-Elmer thermal analyzer in a nitrogen atmosphere from ambient temperature to 600^0C at a heating rate of 15^0C per minute.

Elemental Analyses-It was performed on a Perkin-Elmer 240C elemental analyzer.

Solubility and chemical resistance-Solubility of the films (PF_3) in both cases was checked by immersing the film strips (about 50 mg in weight) at 30^0C and 60^0C in various solvents. The change in weight was noted.

Biological Screening:

Metallopolymers constitutes a class of materials that is attracting increasing attention due to their biocidal properties.Some biodegradable and non-biodegradable polymers have been reported as a drug delivery system.[9] Many metal containing polymers have antimicrobial action of metal containing alloy films were carried out against two bacterial strains viz-Escheria coli and Staphylococcus aureus and two fungal species viz-Aspergilluus niger and Aspergilluus flavus using two fold serial dilution method. In this method graded dilution of test compound in a suitable nutrient medium are inoculated with the organism under suitable conditions in an incubator. The meet peptone agar was used as the growth medium for microorganisms. The tests were evaluated after 24 hours incubation at 37^0C for bacteria and 96 hours incubation at 28^0C for fungi. All the solutions of test compounds were prepared by dissolving 01 mg/ml in propylene glycol and sterilized by adopting the usual method in autoclave. The zones of inhibition based upon zone size around the discs were measured.

RESULT AND DISCUSSION

Appereance of films-The films were transluscent, soft and white in colour.

Fourier Transform infrared analysis- The spectra show the characteristic infrared absorptions aromatic C-H (str), C-H(ben) and C=N at 3200, 600-700 and 2210cm^{-1} respectively[10] (Silverstein.,Wiley Publ.2001).

The polymerization of calcium methacrylate was confirmed from the spectra by band broadening absence of C=C group stretching bands and decrease of intensity of CH_2 wagging vibrations. The spectra show the characteristic infrared absorptions of metal methacrylate.The due to a strong asymmetric and a weak symmetric stretching mode of carboxylate ion close to 1570 and 1400 cm^{-1}

Nuclear magnetic resonance spectra- The chemical shift at 1.9 δ is due to aliphatic protons. The methoxy protons of ester group give signals at 3.4 δ and 3.7 δ for calcium polymethacrylates containing alloy film. The spectral pattern of all the polymer alloy films in the same series was almost same.(figure-1)

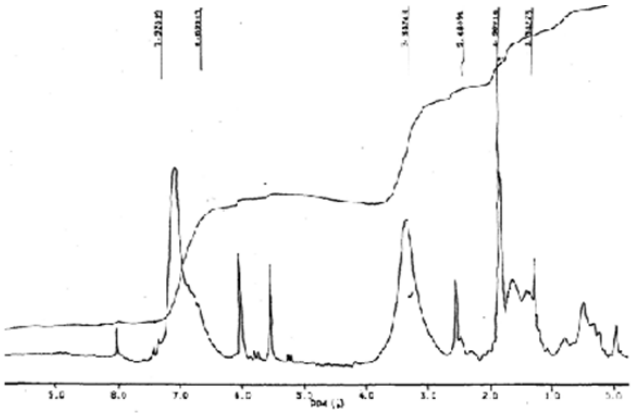

Figure-1 nmr spectra of calcium containing polymer films

Table-2: Gel Permeation Chromatography Data

Polymer film code	Mw	polydispersity	Intrinsic viscosity(^{0}C)
PC1	1,39,931	2.6	0.228
PC2	1,42,920	2.65	0.242
PC5	1,68,963	2.78	0.245
PC6	1,29,724	2.28	0.207

Molecular weight determination- Molecular weight of the films is depicted in table-2. The results indicate that the polymer alloys are of high molecular weight and broad molecular weight distribution.

Thermogravimetry- The thermal degradation of polymer alloy film were studied in the range 30-600^{0}C, under nitrogen atmosphere. The result showed that metal polymethacrylate containing polymer alloys films exhibit high temperature resistance.[11] reported Tg of sty-AN-chromium acrylate terpolymer at 96^{0}C.

The TGA curves of polymer alloy films are wider and show that the weight loss occurs in more than two steps. The first weight loss indicates the evaporation of water. The second loss occurs above 385^{0}C with a maximum decomposition rate at 457^{0}C and 489^{0}C for polymer alloy films containing calcium polymethacrylates. It was observed that the initial temperature for second stage degradation is higher with higher MMA content in polymer film. Table-3

Table-3:Thermogravimetric analysis Data

Polymer film code	IDT (^{0}C)	Decomposition temp. at different weight loss (^{0}C)			FDT (^{0}C)
		50%	75%	90%	
PC1	120	388	391	410	450
PC2	130	390	398	418	457
PC5	95	390	407	427	435
PC6	110	375	387	398	489

Comparison of polystyrene (PS), PMMA, PAN,poly(St–MMA) and poly(St–MMA–AN) with respect to thermal stability of the polymer was made .All the polymerizations are initiated by *p*-NBTPY except that of PAN,[12]which was initiated by AIBN.(Figure-2)

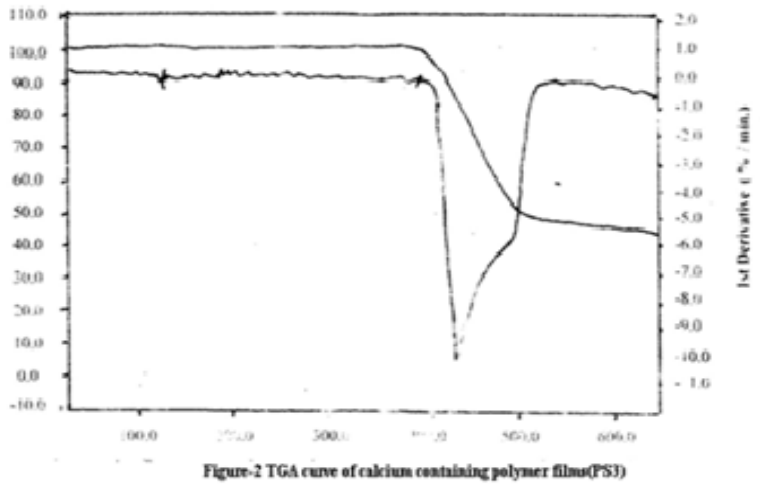

Figure-2 TGA curve of calcium containing polymer films(PS3)

Elemental Analyses- Nitrogen percentage in the polymer alloy films has been calculated. The values were 4.54 and 4.98 for Polycalcium methacrylate.The containing polymer alloy film (PC_1, PC_3) respectively. The results for metal methacrylate.The containing polymer alloy films are summarized in table-4.

Table 4: Elemental analysis Data

Polymer film code	Carbon %	Hydrogen %	Nitrogen %
PC1	65.48	6.39	4.54
PC3	66.67	5.61	4.98

Chemical resistance- Polymers are more susceptible to solvent or chemical attack when under stress and/or strain. Stress can be internal, caused during the manufacturing of the product, or due to externally applied loads. The nature and strength of the chemical will affect the amount of damage. While some dilute chemicals will not attack a polymer, more concentrated solutions can do considerable harm.Table:5

Table-5:Chemical resistance of polycalcium methacrylate.The containing polymer film sample PC_3

Solvents	solubility of film sample PC3 at 70^0C
Dimethyl formamide	++
Dimethyl sulphoxide	+-
Ethyl acetoacetate	++
Carbon Tetrachloride	++
Dioxane	++
Acetone	--
Diethyl ether	--
Sulphuric acid	--
Nitric Acid	--
Hydrochloric Acid	--
Sodium Hydroxide	--
water	--

++ = completely soluble; +- =Partially soluble; -- =Insoluble

The extent of chemical attack on a certain polymer is mainly dependent on the chemical structure of the polymer. In addition, the severity of attack generally reduces with increase in polymer molecular weight, crystallinity, and level of chain branching. The effects of chemical exposure are increased at higher temperatures and with longer periods of exposure.

Biological Screening: All polymer films were tested for their biocidal action. The test species were *E.coli,S.aureus,a.niger* and *A.flavus* using "Agar disc Diffusion method" at a concentration upto 1000ppm and compared with polymer film having no metal content. The polymer film PC4 having highest metal content shows maximum activity against *S.aureus*.(Table-6)Almost all polymer films were ineffective against *A.niger* upto 1000ppm concentration.

Table-6:Biological assays of copolymer films containing poly Calcium methacrylate

Polymer Film Code	Inhibition Zone (mm)			
	E.coli	s.aureus	A.niger	A.flavus
PC1	-	-	-	-
PC2	0.5	2	-	0.5
PC3	0.5	0.5	-	1
PC4	1	1	0.5	1
PC5	0.5	2	-	1
PC6	0.5	2	-	0.5

Antibiological activity of metal containing monomer under study could be referred to a number of causes like injurious effect on the cell wall or cell division, effect on the permeability of cell membrane,chelation and precipitation of the chemicals.(Figure-3)

Figure-3

CONCLUSION

The polymer alloy films of metal methacrylate.The show good resistivity. They were completely soluble in dioxane, dimethyl sulphoxide and dimethyl formamide.Their glass transition temperature is also high.

REFERENCES

[1] Kumar P, Narayan D and Srivastava AK, *Polym Int* 31:221 (**1993**).
[2]. Pandey P and Srivastava AK, (**2002**)*Adv Polym Technol* 21:59.
[3] Shukla P and Srivastava AK, (**1994**),*Macromol Rep* A31:315.
[4] Shukla P and Srivastava AK, (**1996**),*Polym Int* 41:407.
[5] Prajapati K and Varshney A, (**2006**)*J Polym Res* 13(2):97

[6] rajapati K and Varshney A, (**2005**)*J Polym Sci A: Polym Chem* 43:6524.
[7] Oberberger,C.G. and Yamaimoto,N.J,**1966**)*Poly.Sci..,Poly.Chem*.,4,3101
[8]Pomogalio A.D. and Savost'yanov, **1983**,*Chemical reviews*,52(10)
[9]Krishnan P.N, Saraswathi R, Dilip C, Rama Rao N, Sambasiva Rao K.R.S,Raghvendra, *Der Pharmacia Lettre*, **2010**, 2, 5, 83-94
[10] Silverstein RMand Webster FX, (**2001**)*Spectrophotometric Identification of Organic Compounds*, 6th edition. Wiley, New York, Appendix D .
[11] Shukla P and Srivastava AK, (**1994**),*Polymer* 35:4665.
[12] Bhanu VA, Rangarajan P, Wiles K, Bortner M, Sankarpandian M, Godshall D, (**2002**), *Polymer* 43:4841.

.