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SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF COPOLYMER FILMS OF AA-STY CONTAINING POLYLITHIUM ACRYLATE

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ABSTRACT

The copolymer films of acrylic acid and styrene (AA-STY) were synthesized. The films were transparent, brittle and light yellow in colour. The films were permeable and showed adsorption in acetic acid, acetic anhydride and sodium hydroxide. The copolymer films were found to be conducting. The specific conductance of films was found in the range 2.7 x 10^{-6} – 3.0 x 10^{-6} Ω^{-1}. The films were characterized by IR and NMR studies. The films showed good bacterial activity.

Key words: Acrylic acid (AA), Styrene (STY), α, α′-Azobisisobutyronitrile (AIBN)

INTRODUCTION

The demand of new polymeric materials with high thermal and chemical stability has stimulated researchers in many areas of polymer chemistry. The special class of inorganic polymers in which coordination occurs due to interaction between an organic group and a metal atom, is known as coordination polymers. These polymers have properties both of inorganic and organic parts.

Metal organic polymers have found a wide range of technological applications[1] such as molecular separation and the prevention of pollution in air, liquid and water systems, where they can be used as ion exchangers and molecular sieves[2]. Extremely stable open framework metal-organic polymers with expandable structure were reported, which show selective adsorption capability[3].

EXPERIMENTAL

Synthesis of metal acrylates

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The rate of polymerization reactions and the properties of the products are very sensitive to impurities in the monomer, which act as initiators or inhibitors. Therefore, before polymerization, the monomers were purified.

IR and FTIR spectra of metal acrylates, copolymers and alloy films were recorded on Perkin-Elmer 577 spectrometer using appropriate solvents. NMR spectra of polyacrylates, copolymer and alloy films were recorded on AC 300F NMR spectrometers using acetone (D_6) and $CDCl_3$ as solvents and tetramethyl silane (TMS) as internal reference. Electrical conductance of the films was determined with the help of Sinwas type of 07 AT and CL01.07A conductivity meter by using dioxane as a reference liquid.

Purification of monomer and initiator

Styrene (Ranbaxy) of analytical grade was purified according to the method given by Overberger[4], in order to remove the inhibitors present in the monomers. Acrylic acid was freed from inhibitors by vacuum distillation at 333 K. Purification process was used as given by EcK et al[5]. The pure white crystals of α, α′-azobisisobutyronitrile (AIBN) were obtained after crystallization form ethanol (m.p. 102^oC) and were stored in an air tight bottle.

Synthesis of metal acrylates

Preparation of lithium acrylate

3.6 g lithium hydroxide was taken in a flask with 100 mL conc. H_2SO_4 as a solvent with continuous stirring over magnetic stirrer. 3.8 mL acrylic acid was added drop by drop to the solution. The reaction was carried out for 6 hours over magnetic stirrer at room temperature. After completion of the reaction, sulphuric acid suspension was decanted immediately and the product was washed with acetone and dried in air.

Characterization of lithium acrylate

Decomposition point: 220^oC

FTIR Spectrum: Important frequencies (cm^{-1})

νC = O 1630; νC – O 1110; νO – Li 643; νC- H 2927

Preparation of polylithium acrylate

A solution of 1.0 g of lithium acrylate and 50 mL of conc. H_2SO_4 was refluxed with 0.2 g. α, α′-azobisisobutyronitrile (AIBN) and stirred for 6 hours without heating.

Polylithium acrylate was precipitated with the help of acidified methanol and water. It was then dried in a watch glass over water bath.

Characterization of polylithium acrylate

Decomposition point: 200^{o}C

NMR Spectrum: CH_2 = 1.24 δ; CH = 1.46 δ

Synthesis of copolymer

Preparation of acrylic acid-styrene (AA-STY) copolymer initiated by $CaCl_2$

AA-STY and $CaCl_2$ was taken in a hard glass test tube. It was heated on water bath for 7 hours at 80^{o}C using different concentrations of monomers. The contents of the test tube were poured into a petri dish with the help of dioxane and precipitated with acidified methanol and water and then dried on a water bath.

Synthesis of polymer alloys in the form of films

Preparation of films of copolymer of AA-STY (initiated by $CaCl_2$) containing polylithium acrylate

Copolymer films of AA and STY in presence of polylithium acrylate have been prepared using a fixed concentration of 15% by weight of the solute in dioxane. The solution was kept over magnetic stirrer for homogeneous mixing. For preparing metal containing polymer film, different concentrations of polylithium acrylate have also been added. Copolymer of AA with STY have been prepared by polymerizing AA with STY in different weight ratios by varying the concentration of both the monomers (1 : 1, 1 : 1, 2 : 1, 1 : 3, 2 : 2 and 2 : 3) initiated by $CaCl_2$. Results are recorded in Table 1.

Biological screening

Biological screening was done by the most widely used method. It consists of determining the antibacterial activity of concerned polymer by adding in varying concentrations to the culture of test organisms. The biological experiments for determining antimicrobial activity of polymer films were carried out against two non-pathogenic bacteria (viz. *Escherichia coli* and *Staphylococcus aureus*) using agar plate diffusion method.

Procedure

For bacterial study, 24 hours old cultures of *Escherichia coli* and *Staphylococcus* *aureus* were used as the test organism. Sterile filter paper discs of 5 mm diameter impregnated with different concentrations of test compounds (9250, 500 and 1000 ppm) were placed on the surface medium (nutrient agar plate) that had been heavily seeded with test organism. The activity was recorded after 24 hours of incubation at 37 ± 0.1^{o}C and zones of inhibition based upon zone size around disc was measured.

Table 1: Composition of reactants used in the preparation of copolymer films acrylic acid styrene (initiated by $CaCl_2$) containing polylithium acrylate

Temp. = 80^{o}C Time = 7 hours

Polymer film code	Components			
	AA (mol L^{-1})	STY (mol L^{-1})	$CaCl_2$ (mg)	Polylithium acrylate (mg)
PF_1	3.6	5.7	25	-
PF_2	3.6	5.7	25	25
PF_3	7.2	5.7	25	25
PF_4	3.6	17.1	50	50
PF_5	7.2	11.4	25	50
PF_6	7.2	17.1	50	100

RESULTS AND DISCUSSION

The chemical modification of copolymers by alloying with metal containing polymers offers the possibility of combining the desirable applications[6-9]. The following properties were observed in lithium containing copolymer films.

Appearance

The copolymer films were transparent, brittle and light yellow in colour.

Permeability

The permeability of water through film was investigated at room temperature. The films prepared by using different concentrations of polylithium, acrylate, acrylic acid-styrene were found to be permeable in water.

Solubility and chemical resistance

The solubility and chemical resistance of the films was investigated in various organic and inorganic solvents at room temperature and 60°C for two days. The investigated data show that the films were soluble in most of the non-polar solvents but insoluble in polar solvents.

Softening range

The softening range of copolymer films of acrylic acid-styrene with polylithium acrylate are recorded in Table 2 an found in between 105 to 139°C.

Table 2: Physical properties of polymer films of acrylic acid with styrene initiated by $CaCl_2$ containing polylithium acrylate

Polymer film code	Softening range (°C)
PF_1	109 – 129
PF_2	112 – 134
PF_3	110 – 130
PF_4	105 – 128
PF_5	111 – 132
PF_6	114 - 139

Electrical conductance

The electrical conductance of alloy films was determined by using dioxane as a reference liquid. The films are found to be conducting. The specific conductance of copolymer films were found in the range $3.0 \times 10^{-6} – 3.2 \times 10^{-6}\ \Omega^{-1}$.

Adsorption

Film strips (about 25 mg in weight) were dipped in various solvents (acetic acid, acetic anhydride, sodium hydroxide) at 60°C. After relatively short time, the increase in weight due to adsorption was noted.

Elemental analysis

The percentages of carbon and hydrogen in polymer films are -

C = 66.06 X,	H = 5.76%	Found
(66.14%)	(5.91%)	Calculated

Characterization

IR Spectra

The IR spectrum of copolymer film of AA-STY containing polylithium acrylate consists of following bands.

(i) Aliphatic C-H stretching vibration at 2920 cm^{-1} for methyl and methylene groups.

(ii) The C-H bending vibration appears at 1460 cm^{-1}.

(iii) The band at 3045 cm^{-1} show aromatic C-H stretching vibration.

(iv) The peaks at 735 cm^{-1} and 690 cm^{-1} are due to aromatic C-H bending vibrations.

(v) The bands at 1595 cm^{-1} and 1492 cm^{-1} show aromatic C-C stretching vibrations.

(vi) The C=O stretching show a strong a strong ester carbonyl band at 1745 cm^{-1}.

(vii) The C-O stretching band appears at 1220 cm^{-1}.

(viii) Strong and broad band due to O-H stretching appears in the range of 2500-3300 cm^{-1}.

(ix) The bands at 1405 cm^{-1} and 930 cm^{-1} are due to O-H bending.

(x) The metal oxygen band appears at 608 cm^{-1}.

NMR Spectra

The NMR spectra of copolymer film (AA-STY) containing polylithium acrylate gave following informations –

(i) The peaks at 1.25 and 1.45 are due to aliphatic protons, which are methylene and methine protons.

(ii) The peaks at 6.39 – 7.42 are due to aromatic protons

Bactericidal activity

Escherichia coli and *Staphylacoccus aureus* were used as test organisms for bacterial studies. The results are recorded in Table 3.

The bactericidal study of the copolymer films of AA with STY containing polylithium acrylate has shown that it was most active against *S. aureus* in comlparision to *E. coli.* The screening was made at 250, 500 and 1000 ppm.

Table 3: Biological screening of copolymer films of acrylic acid with styrene initiated by $CaCl_2$ containing polylithium acrylate (Inhibition of radical growth in mm).

Time = 24 hours Temp. = 37 ± 0.1°C

Polymer film code	Organisms					
	E. coli (Conc. in ppm)			*S. aureus* (Conc. in ppm)		
	250	500	1000	250	500	1000
PF_1	-	-	-	-	-	-
PF_2	-	-	-	-	0.5	0.5
PF_3	-	-	-	-	0.5	0.5
PF_4	-	-	0.5	-	0.5	1.0
PF_5	-	0.5	0.5	0.5	1.0	1.0
PF_6	-	-	0.5	0.5	1.5	2.5

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