

Synthesis and characterisation of MMA-STY-AN terpolymer films

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ABSTRACT

The present paper deals with the synthesis of terpolymer films of MMA-STY-AN and their physical properties were studied. The films were translucent, brittle and light yellow in colour. The films were found water permeable. The films were soluble in most of non polar solvents. The softening range of alloy films was found in between 89–119 °C. The specific conductance of terpolymer films was found in the range 2.7×10^{-6} - $3.2 \times 10^{-6} \Omega^{-1}$. The films were characterized by elemental analysis FTIR and NMR spectroscopy.

Key words: Methyl methacrylate (MMA), Styrene (STY), Acrylonitrile (AN).

INTRODUCTION

The polymer science is a rapidly growing and vigorously expanding discipline of organic chemistry. In recent years, metal containing monomers and polymers are becoming important¹⁻⁴. The study of structure of metal containing polymers has shown by Raman spectroscopy^{5,6} that in styrene-sodium methacrylate copolymer the cations and anions are aggregated in clusters, particularly in high metal content.

Metal containing polymers obtained by polymerization or copolymerization of metal containing monomer has been used as the components in the preparation of foam plastic⁷, hydrophilic finishing preparations for crease resistant cotton fabrics⁸ and as materials with effective slip.

EXPERIMENTAL

Polymerization reactions and their products are sensitive to impurities present in the monomers. Therefore, it was very essential to purify the monomers, initiators and solvents used before polymerization.

The polymer samples were characterized by spectroscopic techniques. IR and FTIR spectrum of terpolymer of different monomers and alloy films was recorded on Perkin-Elmer 577 spectrometer using appropriate solvents. NMR spectrum was recorded on AC 300F NMR spectrometer using CDCl_3 solvents and TMS as internal standard. Elemental analysis of the synthesized organic compounds was carried out in Perkin-Elmer 240 °C elemental analyzer.

Electrical conductance of the films was determined with the help of 07 AT and CL01.07A conductivity meter using dioxane as a reference liquid.

purification of monomer and initiators

Styrene (Ranbaxy) and methyl methacrylate (Ranbaxy) were of analytical grade and purified according to the method given by Overberger⁹. Purification process of acrylonitrile (BDH)¹⁰ was done by fractional distillation under nitrogen at 76.5-77.5 °C. The pure white crystals of, α, α' -azobisisobutyronitrile (AIBN) initiator were obtained after recrystallization from ethanol, m.p. 102 °C and stored in an air tight bottle.

Synthesis of metal methacrylates

Preparation of lithium methacrylate

3.6 g of lithium hydroxide was taken in a flask with 100 mL conc. H₂SO₄ as a solvent with continuous stirring over magnetic stirrer. 3.8 mL methacrylic 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 washed the product with acetone and dried in air.

Characterisation of lithium methacrylate

Decomposition Point: 250 °C

IR spectra (KBr): (cm⁻¹) ν C=O 1613, ν C-O 1090, ν O-Li 625, ν C-H 3000, ν CH₃ 2910.

Preparation of polyolithium methacrylate

1.0g of lithium methacrylate and 50 mL of conc. H₂SO₄ was taken in a round bottom flask to which 0.2g of AIBN was added. The mixture was refluxed for 6 hours with continuous stirring without heating. The product was precipitated with the help of acidified methanol and water and dried over water bath.

Characterization of polyolithium methacrylate

Decomposition Point: 260 °C

¹H NMR (CDCl₃): δ 0.86 (3H, s, -CH₃), 1.24 (2H, s, CH₂).

Synthesis of terpolymers

Preparation of MMA-STY-AN terpolymer initiated by ZnO

MMA-STY-AN and ZnO was taken in a hard glass test tube and heated on water bath for 10 hours at 80 °C using different concentrations of monomers. The contents of the test tube were poured in to a petridish with the help of dioxane and precipitated with acidified methanol and water, and dried on water bath.

Characterization

IR

ν_{\max} (Nujol mull) (cm⁻¹) 2910 (aliphatic C-H stretching vibration for methyl and methylene groups), 1448 (C-H bending vibration for methyl and methylene groups), 3055 and 3020 (aromatic C-H stretching vibrations), 745 and 690 (aromatic C-H bending vibrations), 1600 and 1490 (aromatic C-C stretching vibrations), 1730 (C=O stretching), 1190 (C-O stretching band), 2330 (C≡N). ¹H NMR (CDCl₃): δ , 0.87, 1.25 and 1.46 (aliphatic methyl, methylene and methine protons), 2.17 (-OCH₃), 6.64-7.43 (aromatic protons).

Preparation of films of terpolymer of MMA-STY-AN (initiated by ZnO) containing polyolithium methacrylate

Terpolymer films of MMA, STY and AN in presence of polyolithium methacrylate have been prepared using a fixed concentration of 15 % by weight of the solute in dioxane. The solution was kept over magnetic stirrer for homogenous mixing. For preparing metal containing polymer films, different concentrations of polyolithium methacrylate have also been added. Terpolymers of MMA, STY with AN have been prepared by polymerizing MMA and STY with AN in different weight ratios by varying both the concentration (1:1:1, 1:1:1, 1:2:1, 2:2:2, 2:1:2, 1:3:1) initiated by ZnO (Table 1).

The terpolymer films were cast by pouring the film solution on a clean dry glass plate and tilting it back and forth to spread the solution on the glass plate kept at room temperature.

Table 1: Composition of reactants used in the preparation of terpolymer films of methyl methacrylate-styrene-acrylonitrile (initiated by ZnO) containing polyolithium methacrylate

Time – 10 hours

Temp. – 80 °C

Polymer film code	Components				
	MMA (mol L ⁻¹)	STY (mol L ⁻¹)	AN (mol L ⁻¹)	ZnO (mg)	Polyolithium methacrylate (mg)
PF ₁	5.5	5.7	3.3	25	-
PF ₂	5.5	5.7	3.3	25	25
PF ₃	5.5	11.4	3.3	50	50
PF ₄	11.0	11.4	6.6	25	25
PF ₅	11.0	5.7	6.6	25	100
PF ₆	5.5	17.1	3.3	50	100

Table 2: Physical properties of polymer films of methyl methacrylate styrene with acrylonitrile initiated by zinc oxide containing polyolithium methacrylate

Polymer film code	Softening range (°C)
PF ₁	92-114
PF ₂	90-109
PF ₃	89-106
PF ₄	96-119
PF ₅	94-116
PF ₆	95-118

RESULTS AND DISCUSSION

There has been significant interest in recent years in the study of terpolymer films, owing to their extensive applications in various fields. Terpolymerisation of methyl methacrylate-styrene and acrylonitrile was carried out at 80 °C by using ZnO as an initiator. The synthesis of films was carried out by stirring 15 % terpolymer solution dissolved in dioxane with different concentrations of polyolithium methacrylate. The following are some important properties studied.

Properties of lithium containing terpolymer films

Appearance

The terpolymer films were translucent, brittle and light yellow in colour.

Permeability

The permeability of water through film was investigated at room temperature. The films prepared using different concentrations of polyolithium methacrylate, methyl methacrylate-styrene and acrylonitrile were found to be permeable in water.

Solubility and chemical resistance

The solubility and chemical resistance of the terpolymer films was investigated in various organic and inorganic solvents at room temperature and at 60 °C for two days. The investigated data showed that the films were soluble in most of non polar solvents viz., ethyl acetate, chloroform, carbon tetrachloride, dioxane, benzene, toluene and acetone and partially soluble in dimethyl formamide, diethyl ether.

Softening range

The softening range of alloy films were found in between 89-119 °C as recorded in table 2.

Electrical conductance

The electrical conductance of alloy films was determined by using dioxane as a reference

liquid. The films were found conductive. The specific conductance of films was found in the range 2.7×10^{-6} - $3.2 \times 10^{-6} \Omega^{-1}$.

Adsorbity

The film strips (about 25 mg in weight) were immersed in various solvents like acetic anhydride, methanol, and nitric acid. Increase in weight due to adsorption was noted. The adsorption of acetic anhydride was found highest as compared to other solvents.

Elemental analysis

The percentage of carbon, hydrogen and nitrogen in polymer films was found as under:

C = 67.57 %, H = 7.08 %, N = 4.10 %
(67.65 %), (7.12 %), (4.15 %)

Thermal behaviour

The thermal curves of polymer films were recorded at the temperature range 20-500 °C. The peak temperature of film was 435.13 °C in the

temperature range 400-500 °C. The total weight loss in the range 20-500 °C was 97 %.

Characterisation of polymer films

The polymer samples were characterized by spectroscopic techniques. FTIR : (cm^{-1}) 2927 (aliphatic C-H stretching vibration by methyl and methylene groups), 1459 (C-H bending vibration by methyl and methylene groups), 3032 (aromatic C-H stretching vibration), 755 and 702 (aromatic C-H bending vibrations), 1611 and 1500 (aromatic C-C stretching vibrations), 2300 (C≡N group), 1736 (C=O stretching), 1209 (C-O stretching), 630 (metal oxygen band). ^1H NMR (CDCl_3): δ 0.90 (3H, s, - CH_3), 1.25 (2H, s, CH_2), 1.41 (methine proton), 1.82 (- OCH_3 group), 6.50-7.42 (aromatic protons).

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