

Synthesis of Emulsion Copolymers of [4-N-Phenylethanamide azo-3-N-(4-nitrophenyl) maleimide, Styrene and Methylacrylate

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Abstract

In order to prepare a new polymeric structure of [4-N-Phenylethanamide azo-3-N-(4-nitrophenyl) maleimide [NPAMI] and polymerization was done by using styrene (Sty) and methylacrylate (MA) as a comonomers via an efficient and effective emulsion polymerization procedure to form an emulsion of copolymer. In this process, monomer [NPAMI] was firstly prepared by using maleic anhydride with other needful, suitable reagents and synthesized by addition mechanism. The structures of monomer and copolymers were confirmed by CHN, FT-IR, ¹H-NMR spectroscopy.

Keyword: Polymeric structure, Copolymer, Maleic anhydride, Styrene, Methylacrylate

1. INTRODUCTION

The synthesis of copolymers containing maleimide compositions, are made by many researchers in last year's using different comonomers moiety and the preparation of these maleimide polymers were done by bulk polymerization. Recently, a new technique of Emulsion polymerization are used to synthesis polymers to overcome of drawbacks of bulk polymerization processes. The emulsion polymerization are known as "products in semi-liquid" whose main properties are determined during polymerization. In this scenario polymerization, increasing uses of emulsions and

public sensitivity to environmental issues, the challenge is to achieve an efficient production of high-quality with high performance materials in a consistent, safe with human, environment-friendly route.

The present paper deals with the synthesis of emulsion copolymerization of [4-N-Phenylethanamide azo -3-N-(4-nitrophenyl) maleimide [NPAMI] and vinyl comonomer derivative styrene (Sty), methylacrylate (MA) and their structures were confirmed by FT-IR and ¹H-NMR techniques.

2. MATERIALS

P-amino acetanilide, maleic anhydride were recrystallized from acetone (Loba Chemie, AR). AIBN (Fisher Scientific, AR), THF, DMF and methanol (Sigma Aldrich, AR) are used without any purification.

3. EXPERIMENTS

A. MONOMER SYNTHESIS BY “CONVENTIONAL METHOD” –

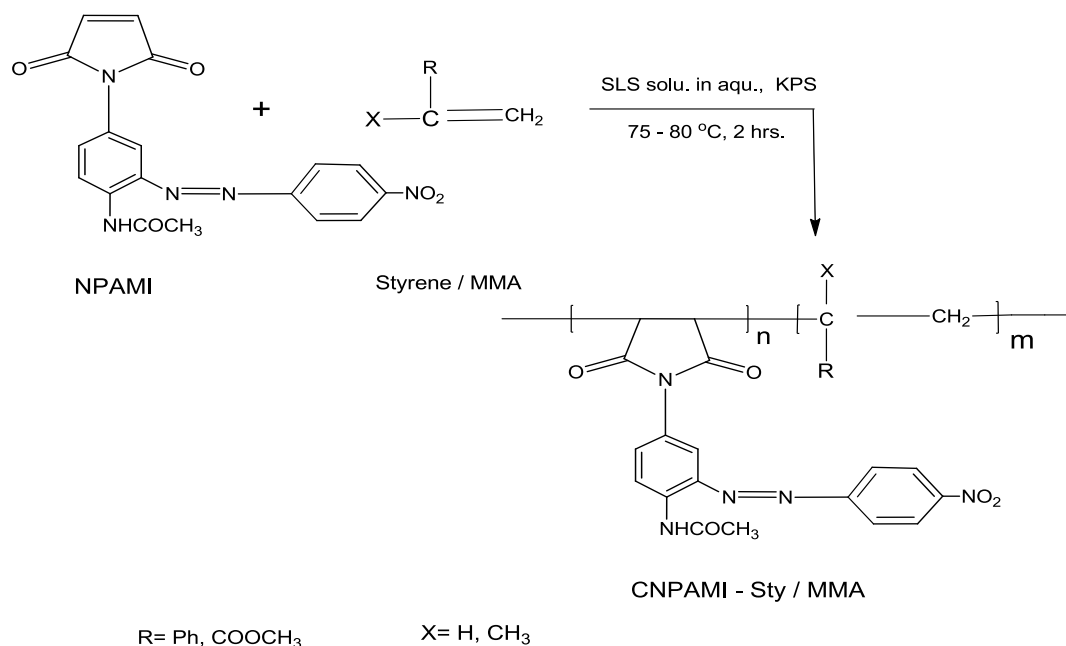
Synthesis of monomer [4-N-Phenylethanamide Azo -3-N-(4-nitrophenyl) maleimide [NPAMI]:

A monomer of [4-N-Phenylethanamide azo-3-N-(4-nitrophenyl) Maleimide [NPAMI] was synthesized according to previously published procedure ^[13].

B. Emulsion Copolymerization –

Synthesis of copolymer [4-N-Phenylethanamide Azo -3-N-(4-nitrophenyl) maleimide-co-Styrene / Methacrylate [CNPAMI-Sty] / [CNPAMI-MA]:

A solution of Sodium Lauryl Sulphate (0.06 M) was placed in a 100 ml three necked flask equipped with a stirrer, a thermometer, a condenser and it was stirred for half hour and then the [NPAMI] monomer solution (dissolved in DMF) and comonomers (Sty and MA) were gradually added at 75 – 80 °C and stirred for two hours. After that the potassium per sulphate (K₂S₂O₈) was used as an aqueous soluble free radical initiator and stirred for 2 hours, know a polymer in form of micelleous state and the final product is isolated by 'breaking' the micelles by the addition of 2% Al₂SO₄ solution to get precipitation. The precipitate was filtered, washed and dried under a vacuum. The products were purified by extraction with methanol and dried again under a vacuum. The conversion ratios of the monomer into both copolymers were over 90%.



Scheme 1: Synthesis of emulsion – copolymers of [CNPAMI-Sty] and [CNPAMI-MMA]

4. INSTRUMENTATION

FT-IR spectra were screened out from perkin-Elmer spectrometer mode RX-I FT-IR equipped with a high purity dried KBr pellets as beam splitter at room temperature. The ¹H-NMR spectra was obtained using a Bruker Avance II 400 MHz NMR spectrophotometer with TMS as an internal standard reference. CHN micro-element analysis were performed by using Thermofinnigan Combustion Analyzer.

5. CHARACTERIZATION

1. 4-N-Phenylethanamide azo-3-N-(4-nitrophenyl) maleimide [NPAMI] monomer- Yield 86%, melting point 148-50 oC; color reddish brown, FT-IR (KBr): 1704 cm⁻¹ (C=O), 3240 cm⁻¹ (N-H), 3095 cm⁻¹ (=C-H, aromatic ring), 2940 cm⁻¹ (C-H asym.), 2830 cm⁻¹ (C-H sym.), 1602 cm⁻¹ (C=O, amide), 1666 cm⁻¹ (CH=CH, C-C Stre., aliphatic), 1372 cm⁻¹ (C-N-C), 1532 cm⁻¹ (N=N), 837 cm⁻¹ and 711cm⁻¹ (Para, Ortho substitution); ¹H-NMR(CD₃OD): 7.19-7.69 (Aromatic), 6.94 -7.20 (HC=CH of Maleimide), 7.66 (Ortho-H of N=N-Ar), 7.68 (Meta -H of N=N-Ar), 10.06 (CO-NH).

2. [4-N-Phenylethanamide azo-3-N-(4-nitrophenyl) Maleimide-co-Styrene] [CNPAMI-Sty] -Yield 85%, melting point 197 °C; color reddish brown, FT-IR (KBr): 1710 cm⁻¹ (C=O), 3320 cm⁻¹ (N-H), 3065 cm⁻¹ (=C-H, aromatic ring), 2920 cm⁻¹ (C-H asym.), 2849 cm⁻¹ (C-H sym.), 1606 cm⁻¹ (C=O, amide), 1395 cm⁻¹ (C-N-C), 1516 cm⁻¹ (N=N), 524 cm⁻¹, 832 cm⁻¹ and 652 cm⁻¹ (Para, Ortho); ¹H-NMR (CD₃OD): 7.30-7.76 (Aromatic), 6.94-7.31 (HC=CH of Maleimide), 7.84 (Ortho-H of N=N-Ar), 8.18 (Meta -H of N=N-Ar), 3.94 {(CH-CH)-n}, 10.06 (CO-NH).

3. [4-N-Phenylethanamide azo-3-N-(4-nitrophenyl)Maleimide-co-methylacrylate] [CNPAMI-MA]- Yield 78 %, melting point 169 °C; color reddish brown, FT-IR (KBr): 1703 cm⁻¹ (C=O), 3323 cm⁻¹ (N-H), 3056 cm⁻¹ (=C-H, aromatic ring), 2900 cm⁻¹ (C-H asym.), 2860 cm⁻¹ (C-H sym.),, 1604 cm⁻¹ (C=O, amide), 1398 cm⁻¹ (C-N-C), 1514 cm⁻¹ (N=N), 834 cm⁻¹ and 744 cm⁻¹ (Para, Ortho); ¹H-NMR (CD₃OD): 7.15-7.66 (Aromatic), 6.65-7.14 (HC=CH of Maleimide), 8.12 (Ortho-H of N=N-Ar), 8.19 (Meta -H of N=N-Ar), 3.69 {(CH-CH)-n}, 10.18 (CO-NH).

The structures of copolymers of [CNPAMI-Sty] and [CNPAMI-MMA] were confirmed by the spectra of these compounds. From the analysis of FT-IR, was found that the absorption band's values, which were observed except that the absorption band of C=C-Ph aromatic and C=C aliphatic at 1666 cm⁻¹, 1645 cm⁻¹ disappeared, confirmed the complete formation of the copolymer compounds.

6. CONCLUSIONS

One monomer and two different copolymer compounds based on [4-N-Phenylethanamide azo-3-N-(4-nitrophenyl) maleimide [NPAMI] have been successfully synthesized and characterized. The use of phosphorus pentoxide [4-N-Phenylethanamide azo-3-N-(4-nitrophenyl) maleimide [NPAMI] (P₂O₅) as a catalyst has decreased the reaction temperature and reaction time from 300 °C to 70-80 °C for the preparation of monomer and use of KPS (K₂S₂O₈) generate free radical to promote the emulsion polymerization reaction in suitable aqueous condition and after de-emulsifying of copolymers, the yield was calculated which is high in production.

ACKNOWLEDGEMENT

The authors would like to thank UGC-Delhi for the financial assistance from fellowship scheme and department of Polymer Science, MLSU for research assistance.

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