

Synthesis and Characterization of Maleic Acid-Butyl Acrylate Copolymers

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In the present work, the polymerization of maleic acid-butyl acrylate using emulsion polymerization has been reported.

Key Words: Maleic acid, Butyl acrylate, Copolymers.

INTRODUCTION

Copolymers of hydrophobic monomers like styrene, alkyl acrylates, acrylonitrile and small amounts (1–10%) of polar unsaturated carboxylated monomers, like acrylic acid (AA), methacrylic acid (MAA), maleic acid (MA) and itaconic acid (IA) are the products of commercial interest due to their applications in paints, adhesives and binders. Recently there has been much interest in the synthesis and investigation of acrylic/methacrylic/maleic acid based copolymers and terpolymers for using them as thickeners in textile printing.

In this paper, polymerization of maleic acid-butyl acrylate, with maleic acid as the major component (53.7–82.3 mol %), using emulsion polymerization technique, has been discussed. No details in literature regarding the true emulsion polymerization of systems containing water miscible monomer as the major component are available. Therefore, in the present work, an attempt has been made to understand the mechanism of Maleic acid (MA)-butyl acrylate (BA) polymerization whether it is emulsion or emulsion and solution simultaneously. The characterization of copolymers (obtained at high conversion), using IR, ^1H NMR and ^{13}C NMR techniques is also reported.

EXPERIMENTAL

Maleic acid (Fluka product) was distilled at 75°C/12 mm of Hg and butyl acrylate (BDH Chemicals, India) was distilled at 50°C/80 mm of Hg before use. A combination of sodium lauryl sulfate (Glaxo Laboratories, India) and Hyoxide AAO, a nonyl phenyl ethylene oxide condensate (Hico Products) was used as the emulsifier. Potassium persulfate and sodium metabisulfite (BDH Chemicals, India) were used as redox initiators.

Polymer synthesis

Maleic acid-butyl acrylate copolymers of varying (MA 53.7–82.3 mol % and BA 17.6–46.3 mol %) were synthesized by using semicontinuous emulsion polymerization technique. The recipe of a 20 g batch is given in Table-1.

TABLE-1
POLYMERIZATION RECIPE (20 g BATCH)

Compound	Weight (g)
Maleic acid	10–16 (0.116–0.956 mol)
Butyl acrylate	4–10 (0.176–0.463 mol)
Sodium lauryl sulphate (anionic emulsifier)	0.4 (2 wt. % of the monomers)
Hyoxide AAO (nonionic emulsifier)	0.6 (3 wt. % of the monomers)
Potassium persulphate (initiator)	0.025 (0.125 wt. % of the monomers)
Sodium metabisulphite (initiator)	0.05 (0.25 wt. % of monomers)
Deionized water	100 (water monomer = 5 : 1)

Time: 4 h; Temperature: 50°C; Atmosphere: nitrogen.

A mixture of anionic sodium lauryl sulphate (2 wt. % of monomers) and nonionic hyoxide AAO (3 wt. % of monomers) was used as emulsifier. Monomers were pre-emulsified using 60% of the total water (60 g), 60% of the total emulsifier, *i.e.*, 0.24 g of sodium lauryl sulphate and 0.36 g of hyoxide AAO and 0.025 g of potassium persulfate. Remainder of the water, emulsifiers and 0.05 g of sodium metabisulfite were charged into a 500 mL round bottom flask, immersed in a constant temperature bath at 50°C and equipped with a mechanical stirrer, a nitrogen inlet, a reflux condenser and a dropping funnel. Monomer emulsion was then added to this polymerization flask slowly, under constant agitation, over a period of 25 min. High degree of conversion (95–98%) could be obtained by carrying out the polymerization for 4 h. Emulsion was immediately broken with cold aqueous NaCl solution, filtered and washed with slightly acidic water and subsequently with *n*-hexane. White polymer obtained was dried in a vacuum oven for 24 h at 70°C.

For determination of reactivity ratios, another set of copolymers using the same recipe but different monomer feed ratios (MA 10–55 mol %, and BA 45–90 mol %) were synthesized. Conversion was kept below 10% in all the cases.

Reactivity ratio determination

Reactivity ratios of MA-BA pair were determined using the procedure based on the statistically valid error-in-variables model (EVM), with the help of RREVM computer program which takes into consideration the errors in determining the composition of comonomers in the copolymer and in the feed. The input parameters for this program are the composition of one monomer in feed as well as in copolymer and the initial estimate of reactivity ratios (obtained from Kelen-Tudos method). The copolymer composition was determined using ¹H and NMR.

Concentration of monomers in the aqueous phase

Maleic acid being a water miscible monomer may get partitioned in favour of aqueous phase leading to deviation from emulsion polymerization mechanism. In order to ascertain the same, the concentration of both the monomers, *i.e.*, maleic

acid and butyl acrylate, in the aqueous phase, before emulsion polymerization was measured. Monomer-water mixture containing different proportions of two monomers (MA 10–75 and BA 25–90 mol % were prepared and stirred for 4 h. After equilibrating for 8 h, aqueous and organic layers were separated and the aqueous content, using gas chromatographic technique. Nucon 5700 gas chromatograph with 10% DEGS (diethylene glycol succinate) column was used for this purpose. Oven temperature was 200°C and FID mode was used for detection.

Polymer characterization

Elemental analysis: Elemental analysis of the copolymers was carried out using Carlo-Erba 1106 elemental analyzer to determine the carbon and hydrogen content of these copolymers.

Acidimetric titrations: Concentration of these copolymers was determined by acidimetric titration of 0.5% polymer solution in methanol against standard NaOH solution with phenolphthalein as an indicator.

Infrared spectral studies: IR spectra of MA-BA copolymers were recorded in KBr pellet using a Nicolet 5DX FTIR spectrometer. The KBr pellets were prepared by grinding 3 mg of the sample with 197 mg KBr in a mortar and then compressed to get a pellet.

¹H NMR studies: ¹H NMR spectra of all the copolymers were recorded on a JEOL JNM FX100 spectrometer operating at 99.55 MHz. Spectra were recorded at 90°C. DMSO-d₆ was used as a solvent and 5% solutions were prepared. Tetramethylsilane was the internal standard. 50–100 free induction decays were accumulated using a pulse width of 21 μs, an acquisition time of 4 s and a spectral width of 1200 Hz (12 ppm).

Proton decoupled ¹³C NMR studies: ¹³C (¹H) NMR spectra were recorded on a Bruker 270 MHz spectrometer using DMSO + DMSO-d₆ as a solvent. All the spectra were recorded at 90°C and the chemical shifts are reported downfield to tetramethylsilane (TMS). Conditions of recording the spectra are as under:

Frequency:	67.5 MHz
Pulse repetition time:	2.0 s
Pulse width:	15 μs

Calculations regarding the fractional peak area measurement were made, using a Lorentzian shape curve fitting computer program on ICL-3960 computer system.

Intrinsic viscosities: Intrinsic viscosity of all the copolymers was measured using an Ubbelohde viscometer. 0.5% solution of copolymers in methanol was used. The measurement was carried out in a thermostat at 30 ± 1°C.

The solvent flow time was first measured (*t*₁). 30 mL of the polymer solution was taken in a viscometer and its flow time was measured. The average of five readings was taken as the time of flow of solution (*t*₂). The solution was then diluted by progressive addition of the solvent. Flow time was measured at each concentration (g/dL).

$$\text{Relative viscosity } (\eta_r) = \frac{t_2}{t_1}$$

$$\text{Specific viscosity } (\eta_{sp}) = \frac{t_2 - t_1}{t_1}$$

$$\text{Intrinsic viscosity} = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c}$$

$[\eta_{sp}/c]$ was plotted against concentration; the value of $[\eta_{sp}/c]$ at zero concentration was taken as the intrinsic viscosity.

RESULTS AND DISCUSSION

As can be seen from the polymerization recipe (Table-1), a very high amount of mixed emulsifier (5% on the weight of monomers) containing 0.6 part hyoxide AAO and 0.4 part sodium lauryl sulphate, had to be used for obtaining a stable emulsion. Preliminary investigations showed that sodium lauryl sulfate alone was insufficient to produce a stable emulsion, even when its concentration was increased from 0.4 to 2 wt. % of the monomer.

The stability of an emulsion is dependent on several factors like reaction temperature, chemical nature and concentration of the monomers in the emulsion, concentration and chemical nature of the surfactants and stirring speed during the polymerization. Lock *et al.*² have reported that flocculation of the particles can occur if pre-existing particles attain a critical size at which they are no longer stable. This flocculation will not occur if there is sufficient adsorbed surfactant.

HLB value (hydrophilic-lipophilic balance) of an emulsifier decides its suitability for different systems. HLB value of 8–15 has been found to be suitable for an oil-in-water system. On the basis of HLB value, nonionic emulsifier, hyoxide AAO (a nonyl phenyl ethylene oxide condensate), having a HLB value of 12.8, was chosen and used (up to 3% on the weight of monomers) for the present system, but no improvement in the stability of the emulsion was observed. However, when a combination of anionic sodium lauryl sulfate and nonionic hyoxide AAO was used, an emulsion, stable for more than 6 months was obtained in all the cases except the one formulation containing 82.3 mol % MA (in feed), which showed a tendency towards coagulation. Similar observation was made by Uglestad *et al.*³ in the emulsion polymerization of styrene, where the significant differences were found in the stability of the emulsion obtained with the sodium lauryl sulfate-cetyl alcohol combination and sodium lauryl sulfate alone. The dependence of the volumetric growth rate of polystyrene particles in a continuous loop reactor under light levels of sodium lauryl sulphate (SLS) has also been studied. The steady state cumulant diameter depends on an order of 0.24 for SLS concentration.

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