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Copolymers of Poly(butyl acrylate): Synthesis, Characterization and Compositional Analysis

ACHINTA MEDHI, ANJANA DHAR, KARABI SARMAH, PARAMITA DUTTA and DHRUBA J. HALOI*

Department of Chemistry, Bodoland University, Kokrajhar-783370, India

*Corresponding author: E-mail: dhruba2k3@gmail.com

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This investigation reports the synthesis and characterization of colloidal latices of butyl acrylate (BA) and its copolymers with styrene (Sty) and acrylonitrile (ACN). The copolymers of BA with Sty, P(BA-*co*-Sty) and with ACN, P(BA-*co*-ACN) were synthesized *via* emulsion polymerization using two different thermal initiators, ammonium persulfate (APS) and potassium persulfate (KPS). Sodium dodecyl sulfate (SDS) was used as surfactant in both the cases. The polymerizations were carried out at 70 ºC for 0.5 h. Attempts had also been made to prepare copolymers with different monomer composition. The progress of the polymerizations with time was monitored by measuring the conversion of monomers gravimetrically. The prepared lattices were characterized by GPC, UV-Vis, FT-IR and ^{1}H NMR analyses. All the prepared lattices were transparent as evident by the UV-visible analysis. The FT-IR and ^{1}H NMR analysis of the purified copolymers confirmed the successful preparation of the copolymers. The molar composition of the co-monomers in the copolymer was calculated by ^{1}H NMR analysis.

Keywords: Emulsion, Acrylate copolymer, Butyl acrylate, Polymerization.

INTRODUCTION

Emulsion is a useful commercial technique to prepare high molecular weight polymer with continuous rapid rate of reaction. There is wide range of applications of polymer lattices prepared *via* emulsion polymerization [1-3]. In emulsion, the number of polymer particles produced during the course of reaction influences the progress of polymerization [4]. Emulsion polymerization is a heterogeneous reaction which produces nearly monodisperse polymer latex particles with the use of a surfactant as emulsifier and water as a solvent instead of volatile organic solvents [1,4-6]. Instead of volatile organic solvents, use of water makes this process green which is also considered as one of the major advantages of this process. In this emulsion polymerization, latex is resulted as an end product which finds a variety of applications in adhesives, paints protective coatings, textile products, binders, *etc*. [3,5,7]. In recent years, based on the starting materials used and polymerization strategies, a few synthetic emulsion techniques have been derived. These are now known as macro-, micro- and mini-emulsion. These techniques differ from each other by the polymerization mechanism and the size of the monomer droplets formed.

Microemulsion is an isotropic liquid consisting oil and water phases and stabilized by a surfactant or a combination of surfactant and co-surfactant. Microemulsion is also transparent and thermodynamically stable. The size of the monomer droplets in microemulsion are in the range of 0.1-0.5 microns. Co-surfactant like the one with short-chain alcohols are usually used [8,9]. While in macroemulsion, no co-surfactant is used and monomer droplets are in the range of 1-10 microns. However, mini-emulsion polymerizations are comparatively new. Here nucleation of monomer droplets occurs which leads to a different mechanism, different rate of polymerization and a different final product [9].

These sub groups of emulsion polymerization are widely being investigated to polymerize monomers like styrene [10-14], vinyl acetate [15], acrylates [15-17], acrylics [18-20] in a wide range of temperature (-20 to 200 ºC) [21]. It has also been reported the possible production of polymers with distinct properties, performance characteristics along with the control of heat transfer using this technique [5]. Chieng *et al.* [8] reported the successful preparation of copolymer of methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) in microemulsion. Fontenot & Schork [9] studied the batch macroemulsion and mini-emulsion polymerizations of methyl methacrylate (MMA) and reported that the mini-emulsion was more stable under shear [9]. Hecht *et al.* [22] carried out mini-emulsion polymerization of MMA with different surfactant concentrations and with different energy inputs. They reported that with increase in droplet size and the concentration of the surfactant increases latex stability. Nomura *et al.* [7] reported that the speed of stirring influences the formation of micelle and hence the formation of number of particles during the course of the reaction. Shunmukham *et al.* [23] also studied the effect of stirring on the emulsion polymerization of styrene and concluded that with the increasing speed of stirring, inhibition increases and this decreases the polymerization rate. In this investigation, the synthesis and characterization of colloidal lattices of butyl acrylate (BA) and its copolymers with styrene (Sty) and acrylonitrile (ACN) is reported. The polymerizations were carried out at an intermediate stirring speed of 450 rpm.

EXPERIMENTAL

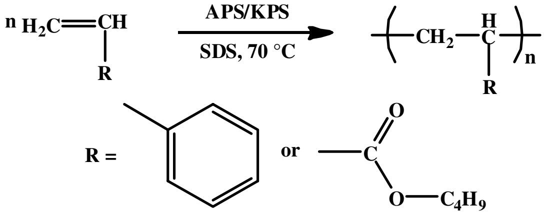
Monomers butyl acrylate (BA) (99%, Aldrich, USA), styrene (98%, Avra, India) and acrylonitrile (Rankeem, India) were used as received. Initiators ammonium persulfate (APS) (98%, SRL, India) and potassium persulfate (KPS) (98%, Avra, India) were also used as received. Surfactant, sodium lauryl sulfate (SDS) (99%, SRL, India) was used as acquired. Double distilled water was used for the emulsion polymerization reaction. Other chemicals like acetone, THF and glacial acetic acid were used as received.

Synthesis of copolymers of butyl acrylate and styrene *via* emulsion polymerization: In a typical emulsion polymerization reaction, distilled water (10 g, 0.50 mol) and the surfactant SDS (0.1 g, 0.35 mmol) were taken in a dry Schlenk tube equipped with a stirrer, a magnetic bar and a rubber septum. The mixture was stirred for 15 min, then BA (1.5 g, 0.0117 mol) and ACN (0.5 g, 0.0094 mol) were then added to the solution. After 1 h of stirring at 450 rpm, APS (0.02 g, 0.80 mmol) was then added to the system. The Schlenk tube was then sealed and nitrogen gas was passed through the mixture for 15 min to remove the dissolved oxygen present in these materials. The polymerization was started by placing the Schlenk tube in a preheated oil bath at 70 ºC. The polymerization was carried out for 30 min. The aliquot was taken out at the end of the of the polymerization to determine the monomer conversion gravimetrically. Same procedure was adopted for the emulsion polymerization reactions where KPS was used as initiator. The latex thus obtained was coagulated by acetic acid, washed thoroughly with double distilled water and then filtered. The residual polymer was then dissolved in THF, re-precipitated from water, filtered and dried over oven at 60 ºC to get the pure polymer ($M_{n(GPC)}$ = 60,960 Da and PDI = 13.62).Thus, the obtained purified polymers were used for GPC, FT-IR and NMR analyses. Same procedure was used for the copolymerization of BA with acrylonitrile.

Characterization: Gel permeation chromatography (GEC) was performed in an Agilent GPC system, using a 50 µL manual sampler, Isocratic pump and 1260 infininity II refractive index (RI) detector. GPC analysis was carried out using THF as eluent at a flow rate of 1 mL/min at room temperature. FT-IR spectra of homo and copolymers were recorded with a Perkin-Elmer FT-IR spectrometer as a thin film on KBr plate at a range of 4000 to 400 cm^{-1}. ^{1}H NMR spectra of homo and copolymers were recorded on 400 MHz Bruker NMR spectrometer using $CDCl_3$ as solvent. UV-visible spectra of latex samples of homo and copolymer were recorded on UV-visible spectrometer scanned in the wave length region from 200-1000 nm.

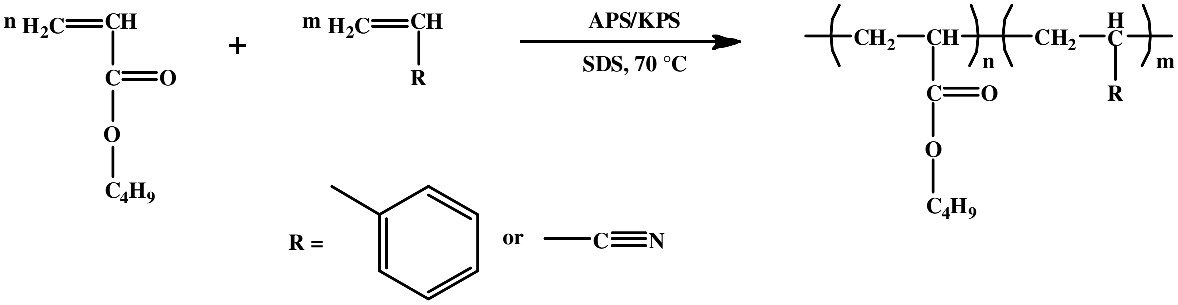
RESULTS AND DISCUSSION

The emulsion copolymerization of butyl acrylate (BA) with styrene (Sty) and acrylonitrile (ACN) (**Schemes I** and **II**) were carried at different monomer feed ratio at 70 ºC.



Scheme-I: Emulsion polymerization of butyl acrylate /or styrene

The polymerization time for all the copolymerizations of BA with Sty was 30 minutes however, for all the copolymerizations of BA with ACN were 60 min. Two different thermal initiators, APS and KPS with different degree of solubility in water were used to initiate these copolymerization reactions and sodium dodecyl sulfate (SDS) was used as surfactant. The copolymerization results are summarized in Tables 1 and 2. The monomer conversion for the copolymerization was determined gravimetrically. In most cases, conversion of monomers was found to be more than 90%. The use of APS as initiator was



Scheme-II: Emulsion copolymerization of butyl acrylate with styrene /or acrylonitrile

TABLE-1
CO-POLYMERIZATION OF BA WITH ACN AT 70 °C USING APS AND KPS AS INITIATORS, COPOLYMERIZATION TIME = 60 min

Sample No.	Monomer feed ratio (wt.%) BA:CAN	Monomer conversion (%)
APS-1	100:0	96
APS-2	75:25	93
APS-3	50:50	95
APS-4	25:75	89
KPS-1	100:0	78
KPS-2	75:25	84
KPS-3	50:50	85
KPS-4	25:75	93

TABLE-2
CO-POLYMERIZATION OF BA WITH STYRENE AT 70 °C USING APS & KPS AS INITIATOR, COPOLYMERIZATION TIME = 30 min

Sample No.	Monomer feed ratio (wt.%) BA:Sty	Monomer conversion (%)
APS-5	75:25	98
APS-6	50:50	97
APS-7	25:75	95
APS-8	0:100	96
KPS-5	75:25	94
KPS-6	50:50	92
KPS-7	25:75	82
KPS-8	0:100	49

found to be more effective than KPS in converting the monomers to copolymer within the same polymerization time.

GPC analysis of the purified copolymers was carried to know the molecular weights of copolymers prepared. The number average molecular weights and corresponding PDIs of the copolymers were found to be very high. However, the uni-modal GPC traces (Fig. 1), which indicates the successful preparation of copolymer free from homopolymers of individual monomer units.

The prepared lattices were found to be stable even after two weeks of preparation. The transparency of the prepared lattices was checked by UV-Vis analysis. Fig. 2 shows the UV-Vis spectra of copolymer lattices of butyl acrylate-based copolymer. All the lattices were found to be nearly transparent. This also indicates the absence of homopolymer and macroscopic phase separation in the lattices. Sparidans *et al.* [24] reported the same kind of observation in their study of copolymers of styrene with methyl acrylate and butyl acrylate.

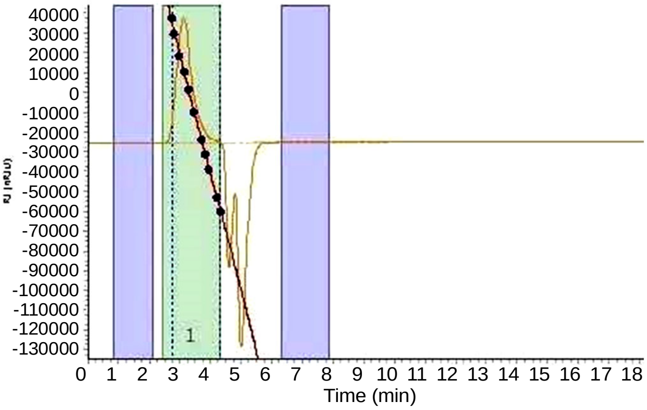


Fig. 1. GPC trace of the copolymer (APS-2)

Fig. 2a shows a shifting of absorbance *versus* wavelength plot towards higher wavelength region for APS-7 as compared to APS-6. This is because of the increase of BA content in the corresponding copolymer.

Fig. 3 shows the FT-IR spectra of poly(butylacrylate-*co*-styrene) (APS-7) and poly(butylacrylate-*co*-acrylonitrile) (APS-2), respectively. In Fig. 3a, the presence of -C-H stretching vibration bands at 3082, 3061 and 3027 cm^{-1} (due to styrene part) and a characteristic >C=O stretching vibration band at 1729 cm^{-1}(due to BA part) confirms the successful preparation of copolymer of butyl acrylate with styrene. Similarly, in Fig. 3b, the presence of an absorption band for >C=O group at 1729 cm^{-1} (due to BA part) and a absorption band for C≡N at 2242 cm^{-1} (due to ACN part) confirms the successful preparation of copolymer of butyl acrylate with acrylonitrile. The results showed that all monomers had participated in the emulsion polymerization reaction.

NMR studies: Fig. 4 shows the ^{1}H NMR spectra of poly(butyl acrylate-*co*- styrene) (APS-7) and poly(butyl acrylate-*co*-acrylonitrile) (APS-2). In Fig. 4a, the resonance at δ 0.87 ppm is attributed to the protons of $-C-CH_3$ moiety and resonances at δ 1.45 and 1.58 ppm assigned to the protons of $-CH_2-$ corresponds to main chain backbone of BA. The resonance at δ 3.63 ppm is assigned to $-OCH_2-$ protons of pendant BA group. The resonances at 6.67–7.12 ppm are due to different aromatic protons of styrene portion of the copolymer. In Fig. 4b, the chemical shift at δ 0.96, 1.65 and 4.02 ppm area assigned to the protons of $-CH_3$, backbone protons of $-CH_2-$ and protons of $-OCH_2$ moiety.

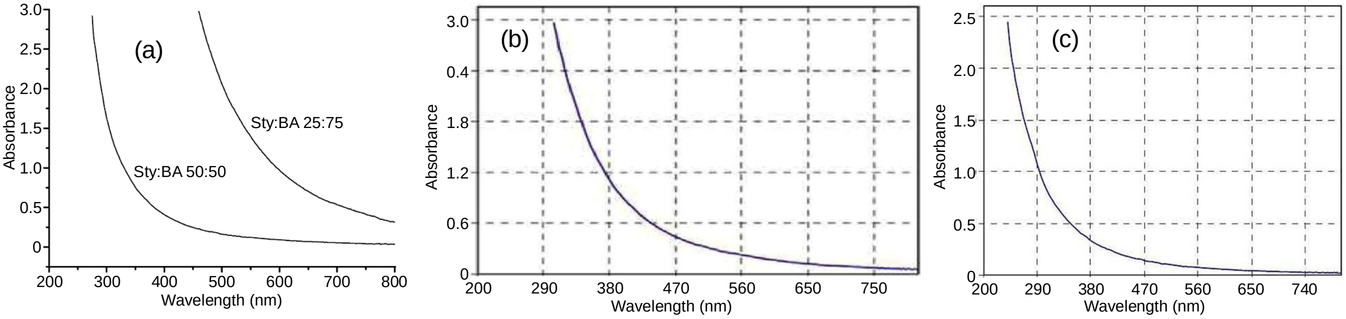


Fig. 2. UV-visible spectra of poly(butyl acrylate-*co*-styrene) latex (APS-6 & 7) (a), poly(butylacrylate-*co*-acrylonitrile) latex (APS-3) (b) and poly(butylacrylate-*co*-acrylonitrile) latex of (APS-2) (c)

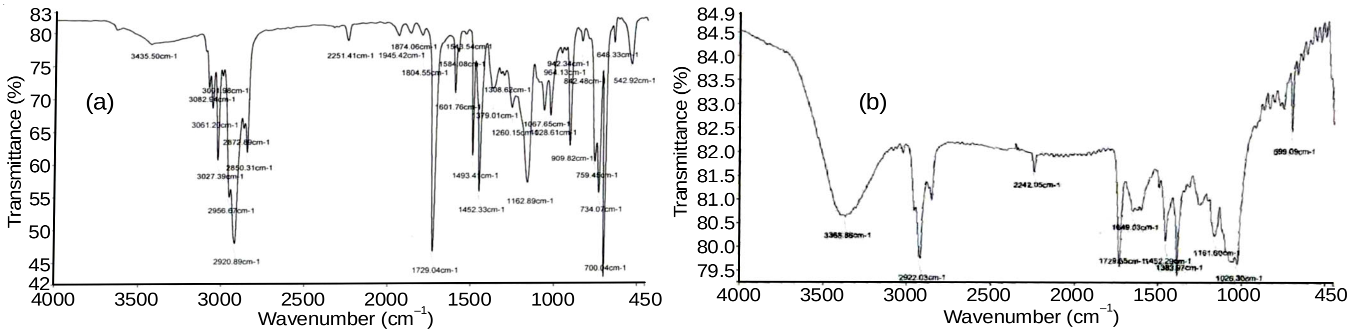


Fig. 3. FT-IR spectra of poly(butylacrylate-*co*-styrene) (APS-7) (a) and poly(butylacrylate-*co*-acrylonitrile) (APS-2) (b)

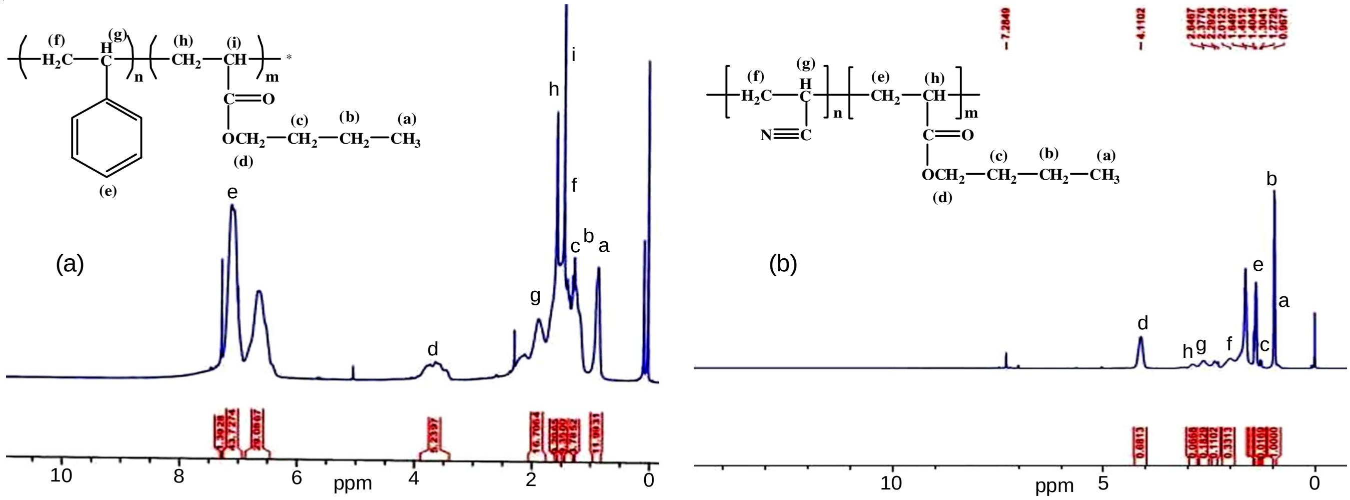


Fig. 4. ^{1}H NMR spectra of poly(butylacrylate-*co*-styrene) (APS-7) (a) and poly(butylacrylate-*co*-acrylonitrile) (APS-2) (b)

Tables 3 & 4 summarize the molar compositions of different monomers in the feed as well as in the prepared copolymers. The monomer compositions in the final copolymers are determined by ^{1}H NMR spectroscopy by using eqn. 1:

$$F_{BA} = \frac{A_{BA}}{A_{BA} + A_{ACN/Sty}} \times 100\% \quad (1)$$

TABLE-3
MONOMER COMPOSITIONAL ANALYSIS OF POLY(BA-*co*-Sty)

Sample No.	Monomer conversion (%)	Monomer composition in feed (mol %)		Monomer composition in copolymer# (mol %)	
		BA	Sty	BA	Sty
APS-5	98	70.9	29.1	79.1	20.9
APS-6	97	44.8	55.2	60.9	39.1
APS-7	95	21.3	78.7	15.2	84.8

#Calculated by ^{1}H NMR

TABLE-4
MONOMER COMPOSITIONAL
ANALYSIS OF POLY(BA-*co*- ACN)

Sample No.	Monomer conversion (%)	Monomer composition in feed (mol %)		Monomer composition in copolymer# (mol %)	
		BA	ACN	BA	ACN
APS-2	93	55.4	45.5	65.1	34.9
APS-3	95	29.3	70.7	48.5	51.5

#Calculated by ^{1}H NMR

where, A_{BA} represents the integrated peak area for one proton of butyl acrylate unit and $A_{ACN/Sty}$ represents the integrated peak area for one proton of acrylonitrile or styrene unit of the same copolymer.

Conclusion

Synthesis of colloidal lattices of homopolymer of butyl acrylate (BA) and its copolymers with styrene (Sty) and acrylonitrile (ACN) were prepared successfully using free radical emulsion polymerization. Two different thermal initiators ammonium persulfate (APS) and potassium persulfate (KPS) were used to initiate the copolymerization reactions. The use of APS as initiator was found to be more effective than KPS in converting the monomers to copolymer within the same polymerization time. GPC analysis of the purified copolymers shows a unimodal GPC trace, which indicates the successful preparation of copolymer free of homopolymers of individual monomer units. The prepared lattices were found to be stable even after two weeks of preparation. All the lattices were found to be nearly transparent as evident by UV-Vis analysis. A shifting of UV-Vis plot towards higher wavelength is also observed with the increase of BA content in the copolymer. FT-IR analysis of pure copolymer confirms the successful preparation of copolymer of butyl acrylate with styrene and acrylonitrile. The final monomer composition in the prepared copolymers were calculated by NMR spectroscopy. Monomer composition in the copolymer is very important for its properties like adhesion, crosslinking and latex stability.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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