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Synthesis and compositional analysis of co- and ter-polymers of butyl acrylate with vinyl acetate and acrylic acid prepared via emulsion polymerization

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This investigation reports the synthesis and characterization of copolymers and ter-polymers of butyl acrylate (BA) prepared via emulsion polymerization. Vinyl acetate (VAc) has been used for the synthesis of copolymer and VAc along with acrylic acid (AA) for the synthesis of ter-polymerswith BA. The polymerizations have been carried out at 70°C for 30 minutes at 470 rpm using two different thermal initiators, ammonium persulfate (APS) and potassium persulfate (KPS) and an emulsifier sodium dodecyl sulfate (SDS). Attempts have also been made to prepare co- and ter-polymers of BAwith varying amounts of monomers. The prepared copolymerswere characterized by GPC, FT-IR, NMR and UV-Vis analyses. The percentage of conversion of monomers to polymer has been calculated gravimetrically. UV-Visible analysis has been used to confirm the preparation of transparent lattices. Furthermore, the incorporation of monomers in the co- and ter-polymers are confirmed by FT-IR and ^{1}H NMR analyses. The molar compositions of the prepared polymers are determined by ^{1}H NMR analysis comparing the areas under the characteristics ^{1}H NMR peaks of the repeating units.

Keywords: Copolymer, Emulsion, Terpolymer, Butyl acrylate, Emulsion polymerization

Emulsion is a liquid-liquid colloidal system where the finely divided droplets are dispersed in a liquid[1]. Emulsion polymerization is a complex process in which the radicals are added into the heterogeneous systems formed by water, monomers, emulsifiers, initiator etc. The initiator used in this process is soluble in the aqueous phase.The polymer chain grows inside the micelle formed by the emulsifier used for emulsification[2].

In the last few decades, emulsion polymerization is growing up as one of the important methodologies for the synthesis of polymers for wide varieties of applications[3]. This versatile and flexible polymerization technique offers us a greener and more convenient route to prepare materials for wide range of applications[4]. Moreover, the wide applications are resulted from their waterborne nature e.g., poly vinyl acetate (PVAc) and vinyl acetate/acrylic copolymer latexes are eco-friendly being capable for waterborne[5,6]. Copolymers of VAc have extensive applications such as in adhesives, carpet backing, exterior and interior paints, and adhesives for clay coatings on paper etc[7]. They also have some unique properties such as excellent mechanical and water resistance properties, which allows them to use even in aqueous phase[8]. Even acrylic based pressure-sensitive adhesives are obtained by using water as a solvent, which can adhere strongly to solid surfaces upon implication of light contact pressure in short contact time[9]. Moreover, latex form of the copolymers of VAc and acrylates are found to be eminent components of both interior as well as exterior paints[10-12]. Also, ter-polymers of VAc have broad applications such as re-moisturable, water soluble packaging etc[13]. Ter-polymer films of methyl methacrylate/styrene/acrylonitrile were found to be water permeable[14].

Many works have been put forward on the syntheses and characterization of copolymers and ter-polymers with different properties for various applications. N. Shinde and his co-workers synthesized polymer using isopropenyl acetate (IPA), BA and methyl methacrylate as monomers and studied their behaviour using FT-IR and GPC analysis[15]. H. Berber and his co-workers prepared water-based VAc-co-BA lattices by using semi-continuous emulsion polymerization technique in presence of oligomeric-NMA[16]. C. F. Jasso-Gastinel and his co-workers synthesized copolymer of Styrene with BA by using same polymerization technique.

The formation of copolymer was confirmed by FT-IR, ^{1}H-NMR and other physical techniques[17]. Yilmaz and his co-workers prepared a few acrylic based copolymers via RAFT mini-emulsion polymerization process and characterized their functional behavior with different physical techniques mostly FT-IR, GPC, ^{1}H NMR and ^{13}C NMR[18]. L. Yang and his co-workers prepared three kinds of ter-polymers which contain N-phenylmaleimide via emulsion polymerization and investigated the mechanical and rheological behaviour of poly (vinyl chloride) blended with the terpolymers[19].

In our investigation, the synthesis and characterization of copolymers of BA with VAc and its ter-polymers with VAc and AA are reported. Two different thermal initiators APS and KPS and the surfactant SDS were used. All the reactions were carried out at 70ºC and at an intermediate stirring speed 470 rpm. The purified polymers were further characterized by GPC, FT-IR, NMR, and UV analyses.

Experimental Section

Materials

Vinyl acetate (VAc) (99%, SRL, India), Butyl acylate (BA) (99%, Aldrich, USA) and Acrylic Acid (AA) (99%, Loba, India) were used as monomers. Ammonium persulfate (APS) (98%, Merck, India) and potassium persulfate (KPS) (98%, Avra Synthesis Pvt., India) were used as initiators. Sodium lauryl (dodecyl) sulfate (SDS) (99%, SRL, India) was used as surfactants. Distilled water was used as a solvent. Other chemicals- Acetone (≥ 99%, EMPLURA, India), Tetrahydrofuran (THF) (99.5%, Rankem, India) and Acetic acid glacial (≥ 99%, Emplura, India) were used in different purposes.

Synthesis of (butyl acrylate-*co*-vinyl acetate) and (butyl acrylate-*co*-vinyl acetate-*co*-acrylicacid)

In a typical co-polymerization or ter-polymerization reaction, distilled water (5g, 0.27 mol) and the surfactant SDS (0.1g, 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, and then varying composition of BA/VAc or BA/VAc/AA (total 2g) was injected to the Schlenk tube. After 15 min of stirring, APS (0.02g, 0.08 mmol) was then added and allowed to stir for 1 hour. The Schlenk tube was then sealed and nitrogen gas was passed through the mixture for 20 min to expel out the dissolved oxygen in it. The reaction tube was then placed in the preheated oil bath and polymerization was carried out at 70°C for 30 min at 470 rpm. The aliquot was taken out at the end of the polymerization and the conversion was determined gravimetrically. Similar approach was adopted for the second initiator KPS (0.02g, 0.07 mmol) with the same composition.

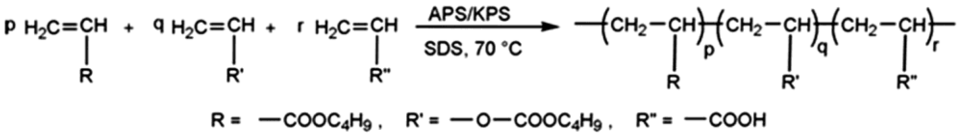
The prepared latex was then coagulated by acetic acid, washed thoroughly with distilled water and was then filtered. The residual polymer was then dissolved in THF, re-precipitated from water, filtered and dried over oven at 60°C to get the pure polymer Thus, the obtained purified polymers were used for GPC, FTIR and NMR analyses. Same procedure was used for the ter-polymerization of BA with VAc and AA.

Characterization

UV-Visible spectra of the purified copolymers and ter-polymers were recorded in the wavelength range of 200-1000 nm on UV-Visible Spectrophotometer. ^{1}H NMR spectra of the synthesized polymer samples were recorded on 400 MHz Bruker NMR spectrometer using $CDCl_3$ as a solvent. FT-IR spectra of purified samples were also obtained as a thin film on KBr plate in the region of 400 to 4000 cm^{-1} and recorded with a Perkin Elmer FT-IR spectrometer. Size Exclusion Chromatography (SEC) was carried out in an Agilent GPC system with configuration comprises of a 50 µL manual sampler, Isocratic pump and 1260 infinity II refractive index (RI) detector. The analysis was performed at room temperature and THF was used as an eluent at a flow rate of 1mL/min in the analysis.

Results and Discussion

In emulsion polymerization, VAc was used for the synthesis of copolymer with BA and VAc along with AA was used for the synthesis of ter-polymers (Scheme 1). The reaction was carried at 70ºC for



Scheme 1 — Emulsion ter-polymerization of butyl acrylate/vinyl acetate/acrylic acid.

30 min with 470 rpm. The initiators APS and KPS with the surfactant SDS was used in emulsion polymerization for the synthesis of copolymer and ter-polymer latices. The copolymerization results are summarized in Table 1 and Table 2. The monomer conversion for the copolymerization was determined gravimetrically. In most cases, the conversion of monomers was found to be more than 90 %. The transparency of the prepared lattices was studied by UV-Visible spectroscopy. Fig. 1 shows the UV-Vis spectra of copolymers of BA/VAc. All the prepared latexes were found to be stable even after few weeks and stable, indicating that there was no macroscopic phase separation and no formation of large amounts of homopolymer. Sparidans *et al.* also reported the same kind of findings in their study of copolymers of styrene with methyl acrylate andBA[20]. In Fig. 1(a), absorbance versus wavelength for BA:VAc (0.0117:0.0056) curve shifts towards higher wavelength in comparison to BA:VAc (0.0078:0.0113) (Fig.1(b)). This shows that with the increase in BA content the particle size increases and curve shows bathochromic shift or red shift.

The incorporation of the monomers was also confirmed by the ^{1}H NMR spectrum. Fig. 2(a) and 2(b) showed the ^{1}H NMR spectra of poly(BA-*co*-VAc) and poly(BA-*co*-VAc-*co*-AA) respectively. The ^{1}H NMR spectroscopy shown in Fig. 2(a) and 2(b) indicate the presence of monomers in the final copolymers and ter-polymers respectively which allows the quantitative determination of the amount of incorporated second monomer unit (Table 3 and Table 4). In Fig. 2 (a), the signals at δ =0.95 ppm and δ =1.99 ppm were attributed to the protons of –CH_3 (a) and –CH_3 (g) of BA and VAc respectively. Signals at δ =1.39 and 1.61 ppm was assigned to the protons of –CH_2– (b) and –CH_2– (c) respectively which corresponds to main chain backbone of BA. In case of VAc, signals at δ =1.50 and 1.58ppm was assigned to the protons of –CH_2– (f) and –CH_2– (i) respectively which corresponds to main chain backbone of VAc. Signals at δ =4.0 ppm attributed to the –O–CH_2– (d) protons of pendant BA group. Signal at δ =1.92 ppm and 5.03 ppm to the backbone proton of –CH– (e) and –CH– (h) of BA and VAc respectively. In Fig. 2(b), the signal at δ =0.94 and 1.97 ppm was attributed to the protons of–CH_3 (a) and–CH_3 (f) of BA and VAc respectively. Signals at δ

Table 1 — Co-polymerization of BA and VAc in emulsion at 70°C using initiators APS and KPS, copolymerization time = 30 min, speed = 470 rpm

Run and Sample	Composition of BA	Composition of VAc	Conversion
No.	(mol)	(mol)	%
A-1	0.0117	0.0056	87
A-2	0.0078	0.0113	97
A-3	0.0039	0.0170	98
K-1	0.0117	0.0056	88
K-2	0.0078	0.0113	94
K-3	0.0039	0.0170	86

*A refers to APS and K refers to KPS

Table 2 — ter-polymerization of BA, VAc and AA in emulsion at 70°C using APS and KPS as initiators copolymerization time = 30 min, speed = 470 rpm

Run and	Composition of	Composition of	Composition of	Conversion
Sample No.	BA (mol)	VAc (mol)	AA (mol)	(%)
A-4	0.0117	0.0048	0.0015	93
A-5	0.0117	0.0035	0.0028	97
A-6	0.0117	0.0022	0.0041	99
K-4	0.0117	0.0046	0.0014	94
K-5	0.0117	0.0035	0.0028	97
K-6	0.0117	0.0023	0.0042	99

*A refers to APS and K refers to KPS

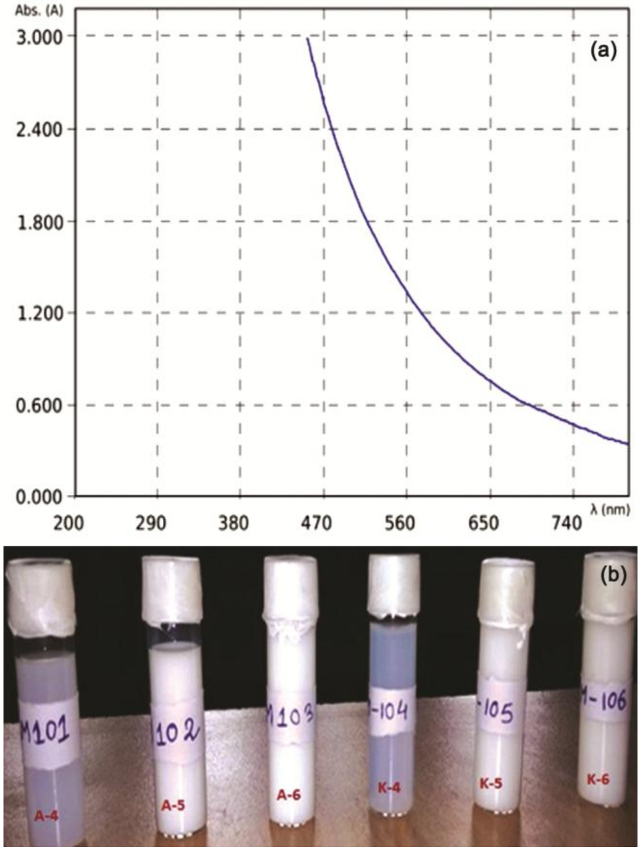


Fig. 1(a-b) — (a) UV-Visible spectrum of latex of copolymer [0.0117/0.0056, BA/VAc] (A-1)&(b) UV-Visible spectrum of latex of copolymer [0.0078/0.0113, BA/VAc] (A-2).

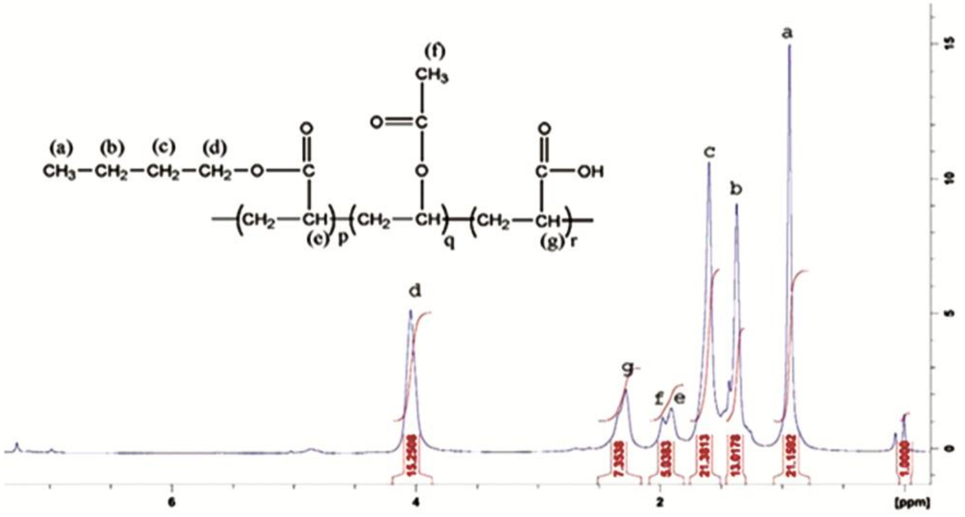


Fig. 2(a-b) — (a) ^{1}H NMR spectrum of Poly (BA-VAc) (A-1) & (b) ^{1}H NMR spectrum of Poly (BA-VAc-AA) (A-4).

Table 3 — Calculated monomer compositions in copolymer by ^{1}H NMR

Sample Number	Conversion (mol %)	Composition in feed (mol%)		Composition in copolymer# (mol %)	
		BA	VAc	BA	VAc
*A-1	87	67.6	32.4	75.6	24.4
A-2	97	40.8	59.2	72.7	27.3
A-3	98	18.6	81.4	8.1	91.9

*A refers to APS and K refers to KPS
#Calculated by ^{1}H NMR

Table 4 — Calculated monomer compositions in ter-polymer by ^{1}H NMR

Sample Number	Conversion (mol %)	Composition in feed (mol%)			Composition in copolymer# (mol %)		
		BA	VAc	AA	BA	VAc	AA
*A-4	93	65	26.7	8.3	62.8	6.9	30.3
A-5	97	65	19.4	15.6	62.3	9.4	28.3
A-6	99	65	12.2	22.8	57.1	36.7	6.2

*A refers to APS and K refers to KPS
#Calculated by ^{1}H NMR

=1.37, 1.60 and 4.04 ppm were assigned to the protons of –CH$_2$– (b), –CH$_2$– (c) and –O–CH$_2$– (d) of BA respectively. Signal at δ =1.90 and 2.28 ppm corresponding to the backbone protons of –CH– (e) and –CH– (g) of BA and AA respectively. In table 3 and table 4 the percentage of molar composition of different monomers in feeds as well as in the prepared copolymers and ter-polymer is shown. The monomer composition in the prepared copolymer and ter-polymer were determined by ^{1}H NMR spectroscopy by the following equation:

$$F_{BA} = \frac{A_{BA}}{A_{BA} + A_{VAc} + A_{AA}} \times 100\ \%$$

where

A_{BA}= the integrated peak area for one proton in poly(butyl acrylate) unit.

A_{VAc}= the integrated peak area for one proton in poly(vinyl acetate) unit.

A_{AA}=the integrated peak area for one proton in poly(acrylic acid)unit.

The formation of copolymer was confirmed by FT-IR spectroscopic analysis. A shift in the C-O-C asymmetric stretching vibration of BA and -CH$_3$ symmetric stretching vibrations of VAc were observed at 1242 cm^{-1} and 2850 cm^{-1} respectively in the FTIR spectra of copolymer of BA and Vac

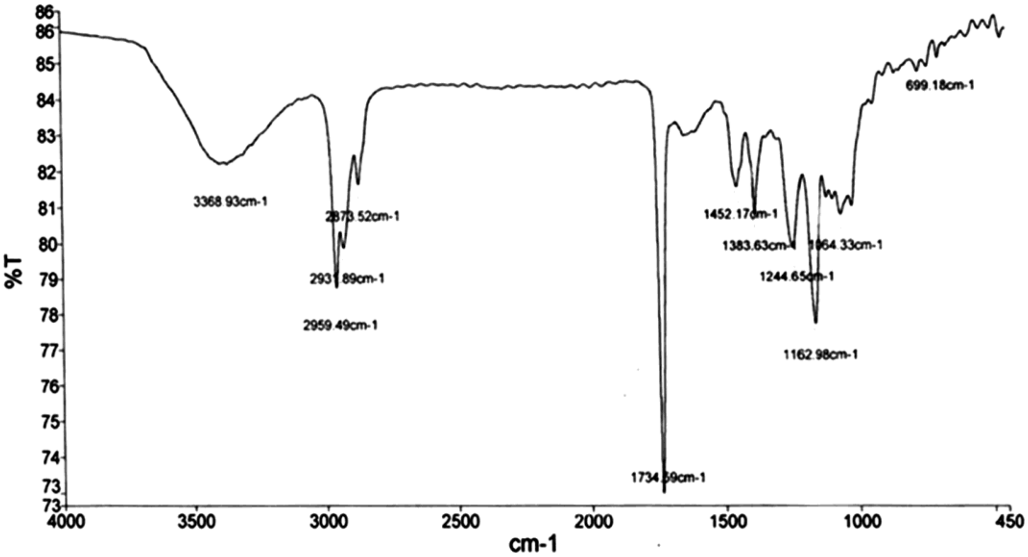


Fig. 3 — FT-IR spectrum of poly (BA-VAc) (A-1).

(Fig. 3). Similarly, the shift in >C=O symmetric stretching vibration of BA and VAc was observed at 1738 cm^{-1} and a shift in the trans -CH wag bending vibration was observed at 946 cm^{-1} in the FTIR spectra of copolymer which confirms the successful preparation of copolymer of BA with VAc. The results confirm that all monomers had participated in the emulsion polymerization reaction.

The synthesized copolymers were purified and analysed by GPC to know their molecular weight. The number average molecular weights of the copolymers were found to be very high with high PDIs. However, uni-modal GPC traces of the copolymers indicated that the prepared copolymers were free from homopolymers.

Conclusion

Colloidal lattices of co-polymer (BA-*co*-VAc) and ter-polymer (BA-*co*-VAc-*co*-AA) of BA were prepared successfully by using free radical emulsion polymerization. To initiate the co-polymerization reaction, two types of thermal initiators APS and KPS were used. All the prepared latexes are found to be stable even after few weeks. The prepared latexes are nearly transparent as evident by UV-Visible analysis. In the UV-Visible plot of absorbance versus wavelength, a shift towards higher wavelength is observed due to the increase in BA content in the copolymer.^{1}H NMR analysis is carried out to know the copolymer and ter-polymer composition via the calculations of areas under the characteristic peaks of the different repeating units present in the copolymer and ter-polymer. FTIR analysis confirmed the successful incorporation of co-monomer in the co-polymer composition. GPC analysis shows a uni-model GPC traces which indicates the successful preparation of co-polymer free from homo-polymers of individual monomers units.

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