Chapter 3:
Synthesis and characterization of vinyl acetate-based co- and terpolymers

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ABSTRACT

This study reports the synthesis and characterization of copolymers and terpolymers of vinyl acetate (VAc) prepared using emulsion polymerization. Vinyl acetate (VAc) has been used for the synthesis of copolymer and VAc along with butyl acrylate and acrylic acid (AA) for the synthesis of terpolymers. The polymerizations have been carried out at 70°C for 30 minutes at 470 rpm using two different thermal initiators APS and KPS and an emulsifier sodium dodecyl sulfate (SDS). Attempts have also been made to prepare co- and terpolymers of VAc with varying amounts of monomers. The prepared copolymers were analyzed 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 latexes. Furthermore, the incorporation of monomers in the co- and terpolymers 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.

3.1. INTRODUCTION

In the last few decades, emulsion polymerization is growing up as one of the significant methodologies for the production of polymers for wide variations of applications.[50] Emulsion is a liquid-liquid colloidal system where the finely divided droplets are dispersed in a liquid.[112] This useful and flexible polymerization technique deals us an environment concern and more suitable route to prepare materials for various beneficial applications.[113] Furthermore, the wide-ranging applications are resulted from their waterborne nature e.g., poly vinyl acetate (PVAc) and vinyl acetate/acrylic copolymer latexes are eco-friendly due to use of water as a solvent.[19,51] VAc copolymers show broad applications such as in adhesives, carpet backing, different kinds of paints, and adhesives for clay coatings on paper etc.[114] They also have some unique properties such as excellent mechanical and water resistance behaviour, which allows them to use even in aqueous phase.[115] 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.[116,117] Moreover, latex form of the copolymers of VAc and acrylates are found to be eminent components of both interior as well as exterior paints.[17,118] Also, terpolymers of VAc have broad applications such as remoisturable, water soluble packaging etc.[119] Terpolymer films of methyl methacrylate/styrene/acrylonitrile were found to be water permeable.[120]

Many works have been put forward on the syntheses and characterization of copolymers and terpolymers with different properties for various applications. N. Shinde and his co-workers synthesized polymer using isopropenyl acetate, BA and methyl methacrylate as monomers and studied their behaviour using FT-IR and GPC analysis.[121] H. Berber and his co-workers prepared water-based VAc-*co*-BA latexes by using semi-continuous emulsion polymerization technique in presence of oligomeric-NMA.[122] The formation of copolymer was confirmed by FT-IR, ^{1}H-NMR and other physical techniques.[123] 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.[124] 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.[125] In our investigation, the synthesis and characterization of copolymers of VAc with BA and its terpolymers with BA and AA are reported. Two different thermal initiators APS and KPS and the surfactant SDS were used.

3.2. PREPARATION

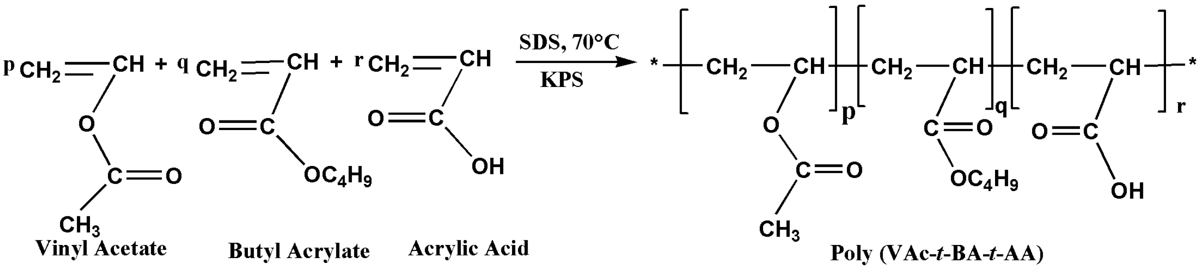
3.2.1. Synthesis of (VAc-*co*-BA) and (VAc-*t*-BA-*t*-AA) via Emulsion

In a typical co-polymerization or terpolymerization 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 minutes, and then varying composition of VAc/BA or VAc/BA/AA (total 2g) was injected to the Schlenk tube. After 15 mins 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 60ºC to get the pure polymer

Thus, the obtained purified polymers were used for GPC, FTIR and NMR analyses. Same procedure was used for the terpolymerization of BA with VAc and AA.

3.3. RESULTS AND DISCUSSION

In emulsion polymerization, VAc was used for the synthesis of copolymer with BA and BA along with AA was used for the synthesis of terpolymers (Scheme 3.1.). The reaction was carried at 70ºC for 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 terpolymer latexes. The copolymerization results are summarized in Table 3.1 and Table 3.2. The monomer conversion for the copolymerization was determined gravimetrically. In most cases, the conversion of monomers was found to be more than 90 %.



Scheme 3.1. Terpolymerization of vinyl acetate, butyl acrylate and acrylic acid

Table 3.1. Co-polymerization of VAc and BA in emulsion at 70 °C using initiators APS and KPS, copolymerization time = 30 minutes, speed = 470 rpm

Run and sample number	Composition of in VAc mol	Composition of BA in mol	% of conversion
A-1	0.0056	0.0117	87
A-2	0.0113	0.0078	97
A-3	0.0170	0.0039	98
K-1	0.0056	0.0117	88
K-2	0.0113	0.0078	94
K-3	0.0170	0.0039	86

*A refers to APS and K refers to KPS

Table 3.2. Terpolymerization of VAc, BA and AA in emulsion at 70°C using APS and KPS as initiators copolymerization time = 30 minutes, speed = 470 rpm

Run and sample number	Composition of VAc in mol	Composition of BA in mol	Composition of AA in mol	Conversion (%)
A-4	0.0048	0.0117	0.0015	93
A-5	0.0035	0.0117	0.0028	97
A-6	0.0022	0.0117	0.0041	99
K-4	0.0046	0.0117	0.0014	94
K-5	0.0035	0.0117	0.0028	97
K-6	0.0023	0.0117	0.0042	99

*A refers to APS and K refers to KPS

Table 3.3. Calculated monomer compositions in copolymer by ^{1}H NMR

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

*A refers to APS and K refers to KPS

#Calculated by ^{1}H NMR

Table 3.4. Calculated monomer compositions in terpolymer by ^{1}H NMR

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

*A refers to APS and K refers to KPS

#Calculated by ^{1}H NMR

The transparency of the prepared latexes (Figure 3.1.) were studied by UV-visible spectroscopy. Figure 3.2. shows the UV-vis spectra of copolymers of VAc/BA. 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 and BA.[126] In Figure 3.2.(a), absorbance versus wavelength for VAc:BA (0.0056:0.0117) curve shifts towards higher wavelength in comparison to VAc:BA (0.0113:0.0078) (Figure 3.2(b)). This shows that with the increase in BA content the particle size increases and curve shows bathochromic shift or red shift.

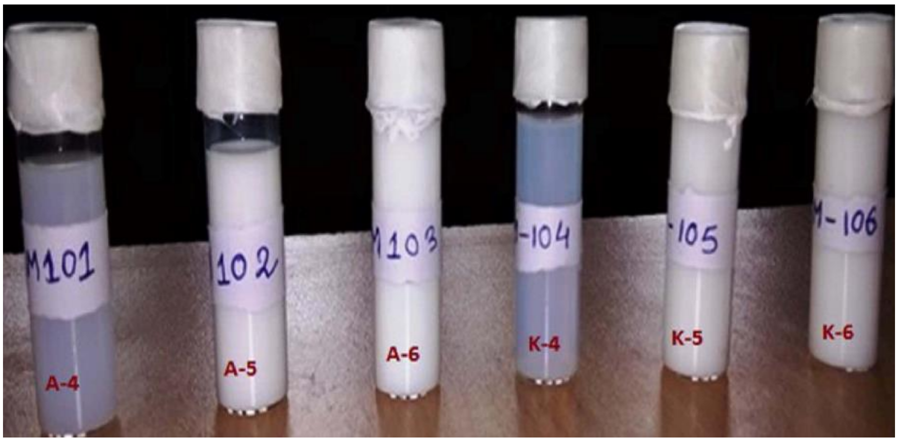


Figure 3.1. Latexes of poly(vinyl acetate-*t*-butyl acrylate-*t*-acrylic acid).

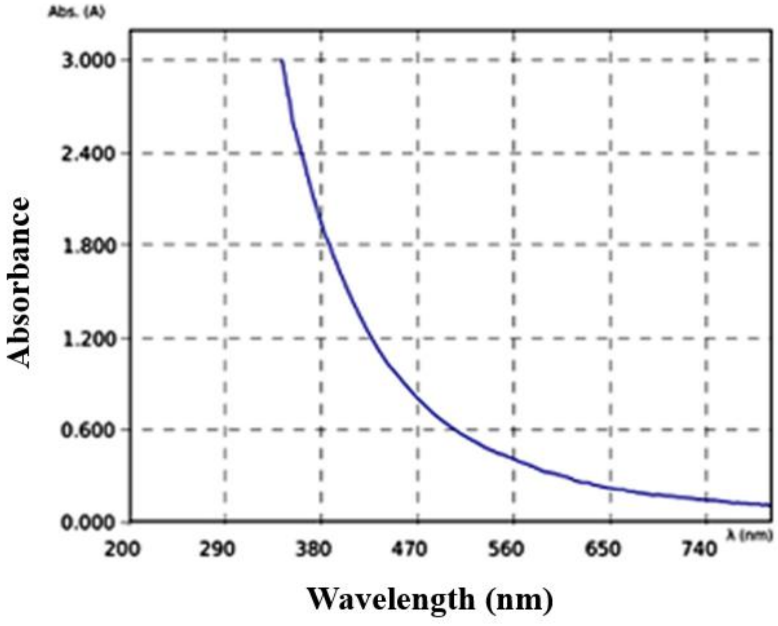


Figure 3.2.(a) UV-visible spectrum of latex of copolymer [0.0056/0.0117, VAc/BA] (A-1).

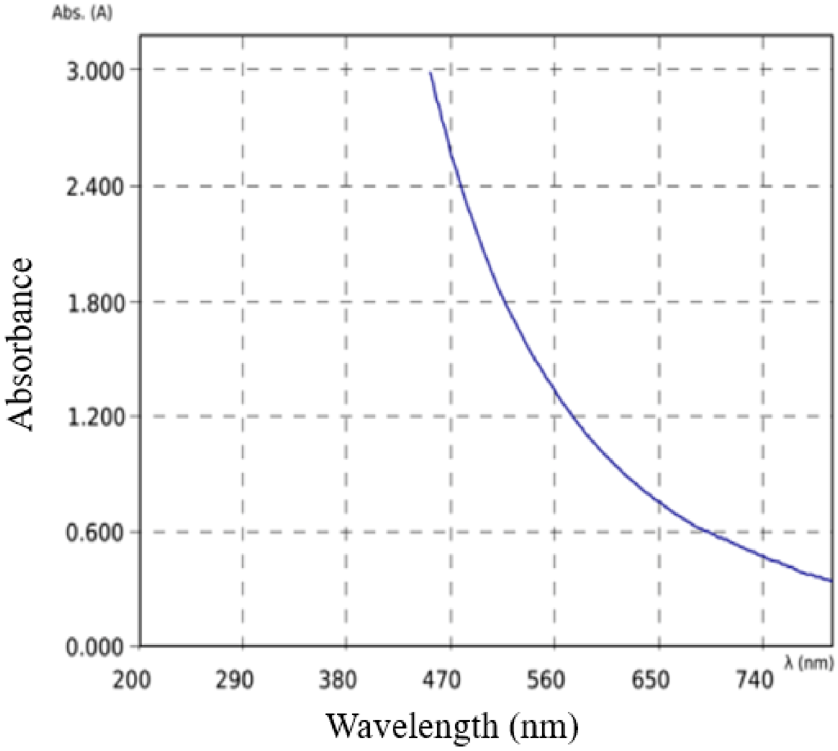


Figure 3.2.(b) UV-visible spectrum of latex of copolymer [0.0113/0.0078, VAc/BA] (A-2).

The incorporation of the monomers was also confirmed by the ^{1}H NMR spectrum. Figure 3.3.(a) and 3.3.(b) showed the ^{1}H NMR spectra of poly(VAc-*co*-BA) and poly(VAc-*t*-BA-*t*-AA) respectively. The ^{1}H NMR spectroscopy shown in Figure 3.3.(a) and 3.3.(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 3.3. and Table 3.4.). In Figure 3.3.(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 Figure 2.3.(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 =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 3.3. and Table 3.4. the percentage of molar composition of different monomers in feeds as well as in the prepared copolymers and terpolymer is shown. The monomer composition in the prepared copolymer and terpolymer were determined by ^{1}H NMR spectroscopy by the following equation:

$$F_{BA} = \frac{A_{BA}}{A_{BA} + A_{VAc} + A_{AA}} \times 100\ \% \qquad \longrightarrow \qquad (3.1)$$

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.

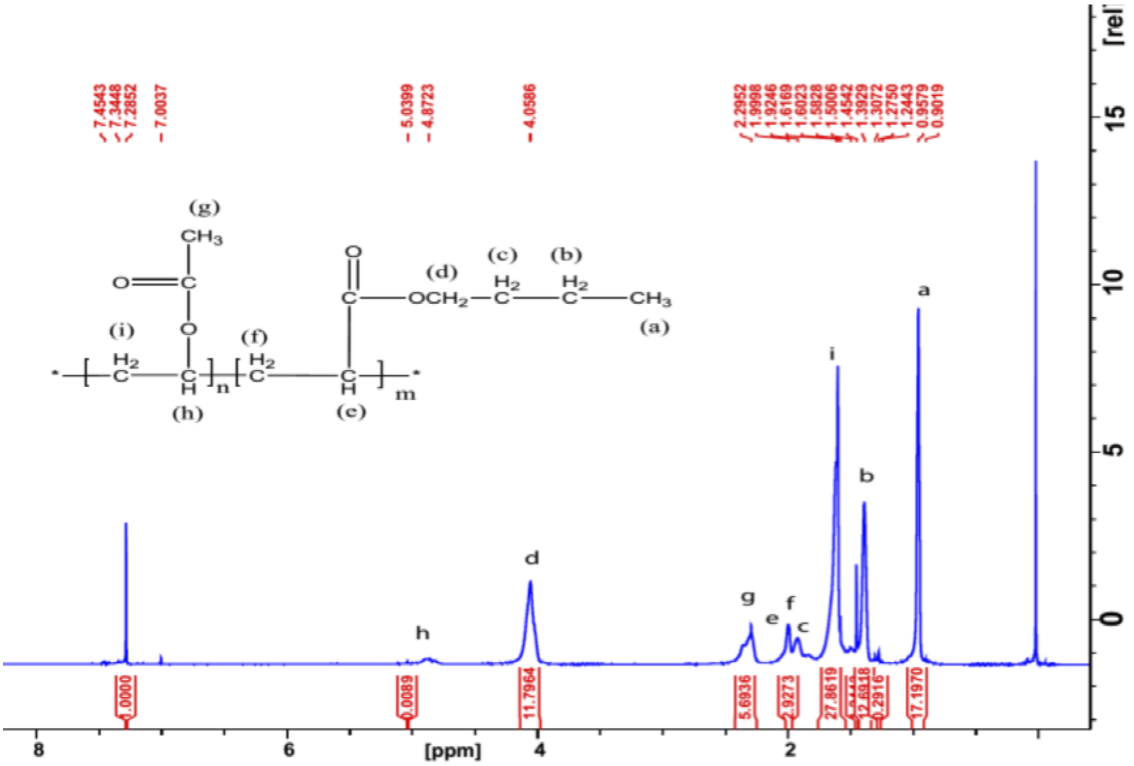


Figure 3.3.(a) ^{1}H NMR spectrum of poly(VAc-*co*-BA) (A-1).

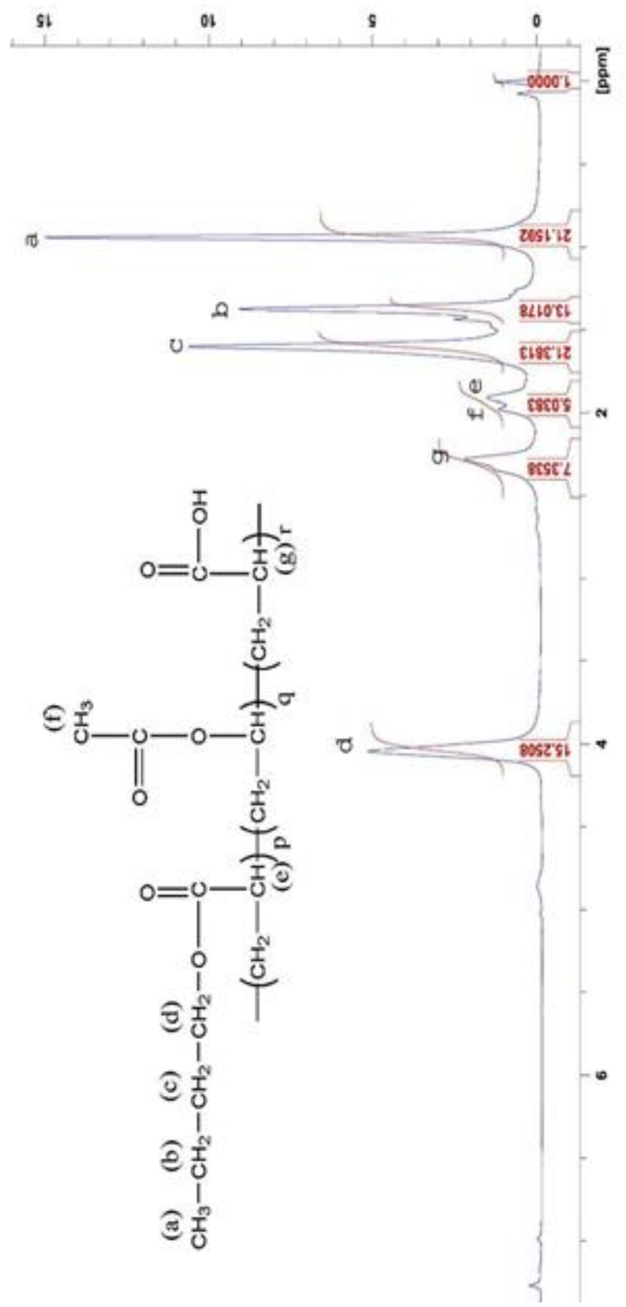


Figure 3.3.(b) 1H NMR spectrum of poly (VAc-*t*-BA-*t*-AA) (A-4).

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 1244 cm^{-1} and 2873 cm^{-1} respectively in the FTIR spectra of copolymer of BA and VAc (Figure 3.4.). Similarly, the shift in >C=O symmetric stretching vibration of BA and VAc was observed at 1734 cm^{-1} and a shift in the trans —CH wag bending vibration was observed at 1064 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.

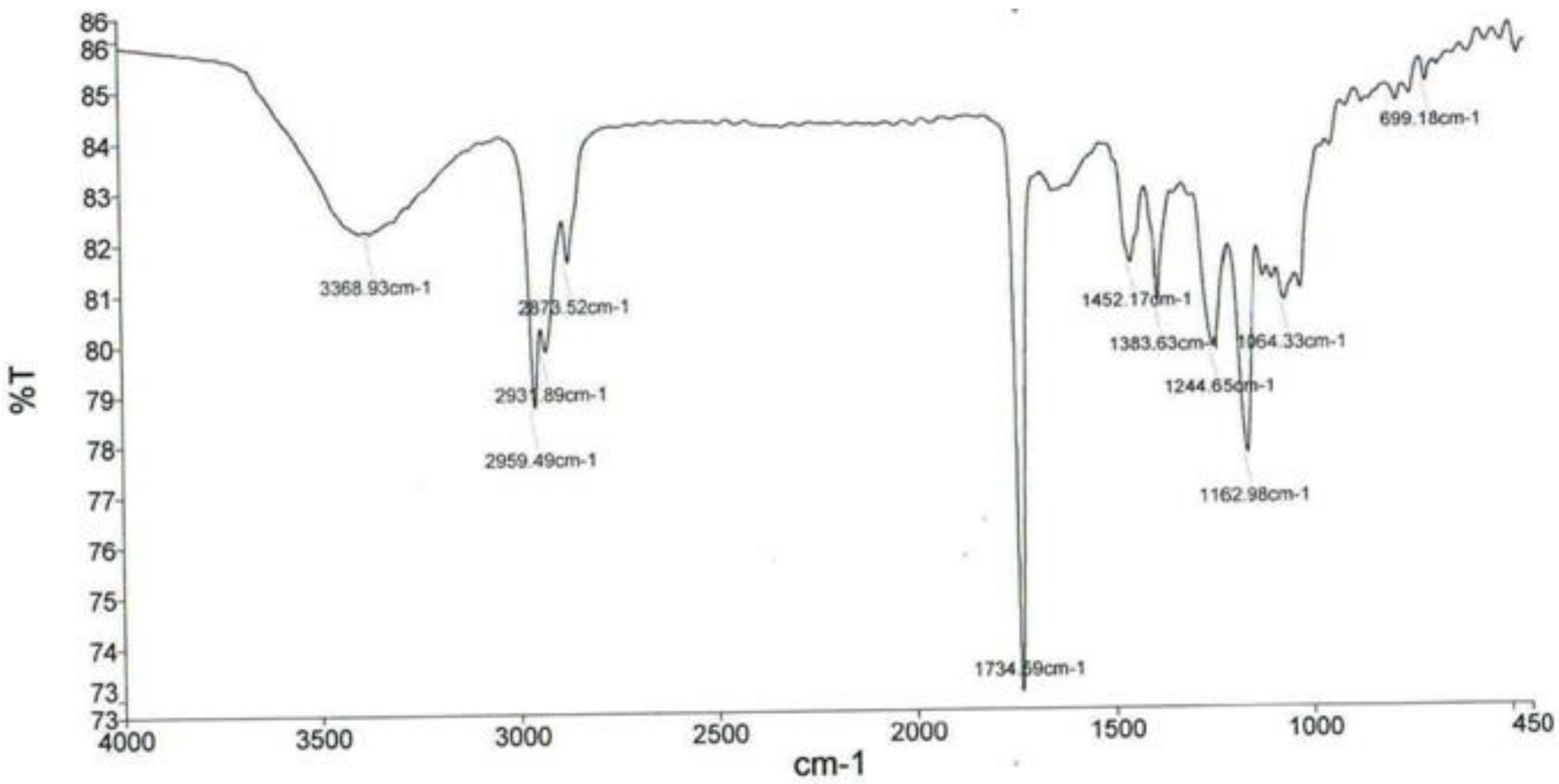


Figure 3.4. FT-IR spectrum of poly (VAc-*co*-BA) (A-1).

The synthesized copolymers were purified and analyzed by GPC (Figure 3.5.) 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.

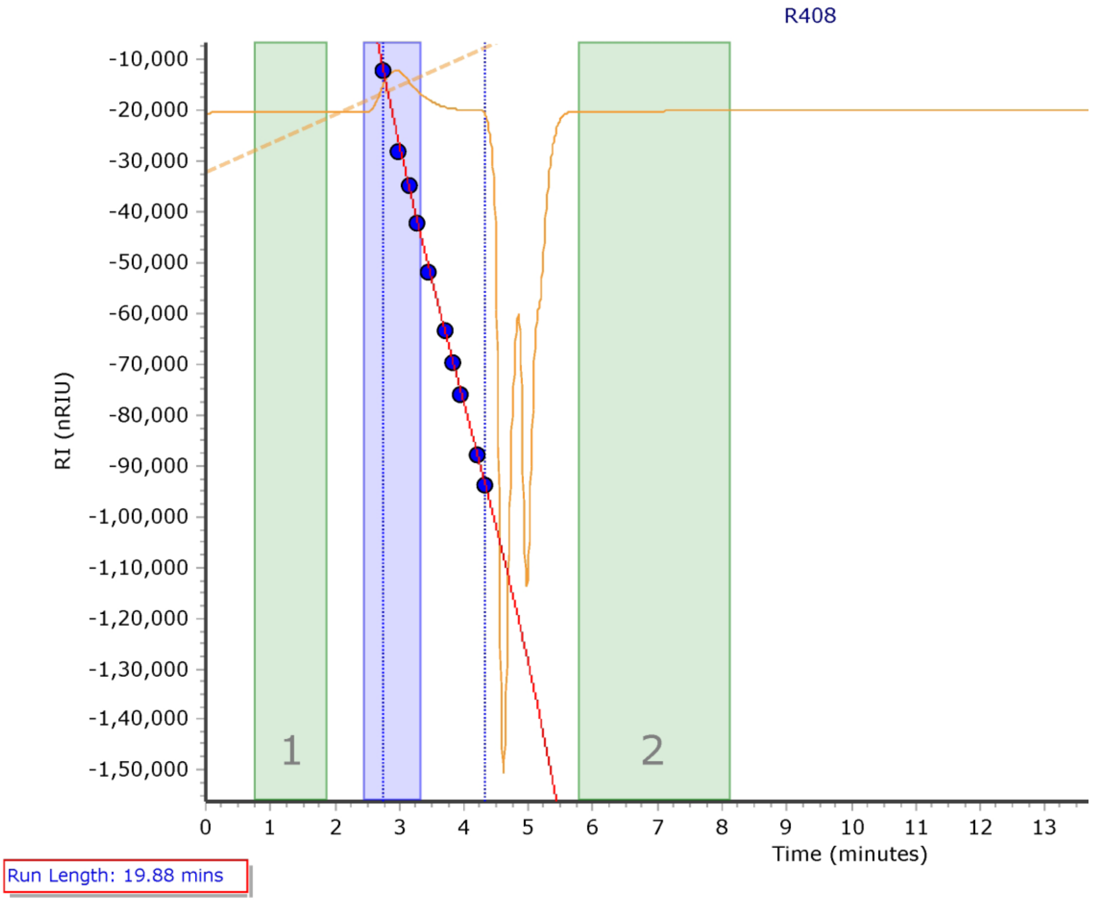


Figure 3.5. GPC trace of the copolymer (A-1).

3.4. CONCLUSION

Colloidal latexes of co-polymer (VAc-*co*-BA) and ter-polymer (VAc-*t*-BA-*t*-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 terpolymer composition via the calculations of areas under the characteristic peaks of the different repeating units present in the copolymer and terpolymer. FTIR analysis confirmed the successful incorporation of co-monomer in the co-polymer composition. GPC analysis shows a uni-modal GPC traces which indicates the successful preparation of co-polymer free from homo-polymers of individual monomers units.