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PREPARATION AND CHARACTERIZATION OF SOME ACRYLIC ACID CHELATING COPOLYMERS BY EMULSION TECHNIQUE

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ABSTRACT

Binary chelating copolymers were prepared by emulsion copolymerization of acrylic acid (AA) with butyl acrylate (BuA), butylmethacrylate (BuMA) and styrene (St) using potassium persulphate/sodium meta bisulphite as a redox initiation system and sodium dodecylbenzene sulfonate as an emulsifier. It was found that the rate of copolymerization was decreased with increasing AA content. Based on the copolymerization data of (BuA/AA), (BuMA/AA) and (St/AA) in emulsion polymerization process, the reactivity ratios of the systems were calculated and discussed. The structures of the designed chelating copolymers were characterized and investigated via spectrophotometric measurements and thermal analysis. Some of the best stable copolymeric emulsions having enhanced physico-mechanical properties were introduced in water-borne paint formulations. The prepared chelating copolymers showed semiconducting properties at room temperature.

Key Words: Chelating copolymer latices; BuMA-co-AA; BuA-co-AA; St-co-AA; Reactivity ratios; Water borne paints; Semiconducting properties

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INTRODUCTION

Much research has been reported concerning emulsion polymerization of vinyl monomers.[1−6] In a previous study by Lu, Ying Chieh et al.[7] the copolymer, comprising 40−90% styrene unit and 10−60% acrylic unit, is manufactured by emulsion polymerization, while continuously supplying the two monomers while controlling unreacted styrene content at $\leq 0.6\%$ in reaction mixture. The copolymers are useful as sizing agents for papers and emulsifiers for rosin or styrene−(meth)acrylic acid ester copolymer emulsions. Thus, a paper coated with an aqueous solution containing 168/72 styrene-acrylic acid copolymer K salt showed Stockigt sizing degree 28.6 s.

An acrylic−styrene copolymer emulsion was prepared by seed polymerization process with St, MMA, BA and AA as raw materials.[8] A systematic experimental and modeling study of several emulsion polymerization systems has been performed. Ten binary and three ternary copolymerizations involving styrene, methyl methacrylate, butyl acrylate, butadiene, vinyl acetate, acrylic acid, and ethylene were studied using different parameters.[9] Redispersable powders, which give emulsifier−stabilized dispersions without the use of protective colloids, are prepared by radical emulsion polymerization of mixtures of vinylaromatic compounds, 1,3-alkadienes or alkyl methacrylates, and unsaturated dicarboxylic acids or anhydrides and drying of the resulting dispersions in the presence of 3−40 phr hydroxy acid. Emulsion polymerization of styrene, butadiene, acrylic acid and unsaturated dicarboxylic acid gave a stabilized dispersion which was mixed with citric acid (polymer−acid ratio 85:15) basified pH 7.[10] The copolymerization for ceramic coating with good prevention precipitation of efflorescence during autoclave recuperation comprises mainly a glycidyl containing acrylic polymer emulsion. Thus, emulsion polymerization of 2-ethylhexyl acrylate, MMA, styrene, glycidyl methacrylate and acrylic acid in the presence of sodium laurate, ammonium laurylsulfate and ammonium water in mixtures of trimethylpentanediol monoisobutyl ether and water gave a primer coat having solid content 10%.[11] All acrylic acid block copolymer precursors can be synthesised via anionic techniques demonstrating predictable molecular weights and narrow molecular weight distribution.[12−14] The surfactant type effect and purity upon emulsion polymerization of styrene and acrylic acid was discussed.[15] Binary and ternary copolymerizations of di(tri-n-butyltin) itaconate (TBTI) with methyl acrylate (MA), ethyl acrylate (EA), n-butyl acrylate (BA), styrene (St) and acrylonitrile (AN) were carried out.[16−18] Emulsion and mini-emulsion copolymerization was carried out with acrylic monomers (methyl methacrylate, butyl acrylate and acrylic acid) in presence of alkyd resin.[19] The kinetics of emulsion copolymerization with acrylic acid were also discussed.[20] The copolymerization of acrylic acid and styrene in a cationic microemulsion made with dodecyltrimethylammonium bromide was reported.[16] Study of the copolymerization parameters of 4-methacrylamidel- methylthiosulfonate with styrene, n-butyl acrylate and acrylic acid,[22] and the copolymerization parameters of N-antipyryl acrylamide with different alkyl acrylates and styrene monomer[23] were reported. The sequence distribution of homogeneous styrene (St)- acrylic acid (AA) copolymers obtained by bulk polymerization was studied by ^{13}C-NMR. The reactivity ratios r (AA) and r (St) were determined by the Kelen Tüdös method.[24]

In our previous studies, we reported the synthesis and characterization of butyl acrylate/vinyl acetate and styrene-BuA copolymers by emulsion techniques for paint applications.[25,26]

The aim of the present study is to prepare and characterise a series of chelating acrylate copolymers for waterborne paints and to throw light on their electrical conductivity at room temperature.

EXPERIMENTAL

Materials

Acrylic acid (AA), butyl methacrylate (BuMA), Styrene (St) and butyl acrylate (BuA) monomers, (14 pp hydroquinone) as well as potassium persulfate (KPS), were supplied by Merck-Schuchardt, Germany. The monomers were redistilled before use and stored at −20°C, while KPS was recrystallized from water by methanol and the final crystals being vacuum dried. Sodium dodecyl benzene sulfonate (SDBS) was a product of the Egyptian Starch, Yeast, and Detergent Company, Egypt. Sodium meta bisulphite (NaMBS) was a product of El-Nasr Pharmaceutical Chemical Company, Egypt. Water used in all experiments was purified by distillation.

Polymerization of Acrylic Acid (AA) Under Emulsion Conditions

The following ingredients were mixed in a 500 mL three-necked flask: water, initiator (KPS/NaMBS), emulsifier (sodium dodecyl benzene sulfonate) and finally acrylic acid (AA) monomer. The polymerization reactions were carried out at 65°C. All experimental were run with mechanical stirring at 500 rpm.

Semi-Batch Emulsion Copolymerization of Acrylic Acid with Styrene (St), Butyl Acrylate (BuA), and Butyl Methacrylate (BuMA)

Copolymerization of acrylic acid with styrene (St), butyl acrylate (BuA) and butyl methacrylate (BuMA) of different feed monomer compositions were prepared by the technique of semi-batch emulsion copolymerization processes. The following ingredients were mixed in a 500 mL three-necked flask: redox pair initiation system KPS/NaMBS (0.27/0.416 gm) and (1 gm) sodium dodecyl benzene sulfonate (SDBS) as an emulsifier were dissolved in distilled water (90 mL). Finally, binary mixtures of (AA with St), (AA with BuA) and (AA with BuMA) of different feed monomer compositions were prepared by adding the acrylic acid monomer dropwise to the hydrophobic monomer in the reaction media. The polymerization reactions were carried out at 65°C for a period of 4 h. The experiments were run with mechanical stirring at 500 rpm.

Instrumental Analysis

IR Spectra

IR analysis for the prepared polymers was carried out using Perkin–Elmer FT-IR, Micro Analytical Unit, Cairo University.

Thermal Analysis

A thermogravimetric analysis (TGA) was made under constant rate of nitrogen using Perkin–Elmer 7 series Shimadzu-TGA 50 H thermal analysis system.

^{1}H-NMR Spectroscopy

The ^{1}HNMR spectra of the prepared polymers were run on a JEOL EX-270 NMR spectrometer, 270 MHz, was used with super conducting magnet Oxford and 5 mm Dual probe head for ^{1}H and ^{13}C- analysis. Typical conditions = spectral width = 4000 Hz for ^{1}H; 32 K data points and flip angle of 45°.

Physico-mechanical Properties of Some Prepared Copolymers

The physico-mechanical properties were measured as described in a previous publication.[27]

Electrical Properties of the Prepared Acrylic Acid Copolymers

The prepared copolymers were precipitated by adding sodium chloride solution to the emulsion latex. The precipitate was then taken, washed several times by hot distilled water to dissolve the emulsifier used, acrylic acid monomer and sodium chloride present. The homopolymer formed of butyl acrylate and butyl methacrylate was then excluded by soxhlet extraction from hexane. The homopolymer of styrene was excluded by soxhlet extraction from toluene. The polymers were then dried in an electric oven at 70°C. The a.c conductivity of the prepared polymers were measured at room temperature for different frequency ranges from (10−100 KHz) using a Stanford Research System Bridge Model SR 720 (USA). Before measurements, the powdered samples were made into pellets of 13 mm in diameter and 1–3 mm in thickness, under pressure of 10 tons/cm^2. The two surfaces of each pellet or sheet were coated with silver paint and checked for good conduction.

Physical and Mechanical Tests of Dry Polymer and Latex Paint Films

Drying time;[28] Adhesion;[29] Hardness;[30] Impact resistance;[31] Ductility.[32]

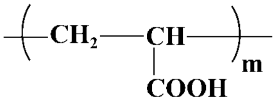
RESULTS AND DISCUSSION

Synthesis and Characterization of Acrylic Acid (AA) Copolymers

Copolymerization of Acrylic Acid and Butyl Acrylate

Acrylic acid copolymerizes with styrene (St), butyl acrylate (BuA) and butyl methacrylate (BuMA) in order to enhance some desired physico-mechanical properties for application in emulsion paints. For this reason, five different copolymers having different concentrations of Butyl acrylate (BuA)/acrylic acid (AA) (series1) Butylmethacrylate (BuMA)/acrylic acid (AA) (series2) and styrene (St)/acrylic acid (AA) (series 3) were prepared using the redox pair initiation system (KPS/NaMBS) at 65°C. The percent of conversion as a function of time is illustrated in Fig. 1.

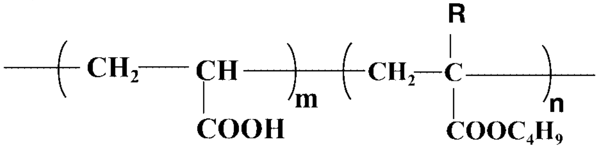
The structure of designed chelating copolymers of (BuA/AA), (BuMA/AA) and (St/AA) and AA homopolymer are shown in the following schemes:



$$-\left(CH_2-\underset{COOH}{\underset{|}{CH}}-\right)_m-$$

Polyacrylic acid (PAA)

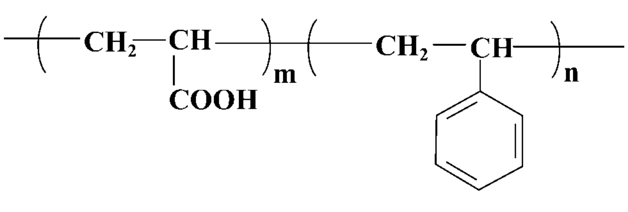
AA/BuA or AA/BuMA copolymers



$$-\left(CH_2-\underset{COOH}{\underset{|}{CH}}-\right)_m\left(CH_2-\overset{R}{\overset{|}{\underset{COOC_4H_9}{\underset{|}{C}}}}-\right)_n-$$

R = H or CH_3

AA/St copolymers



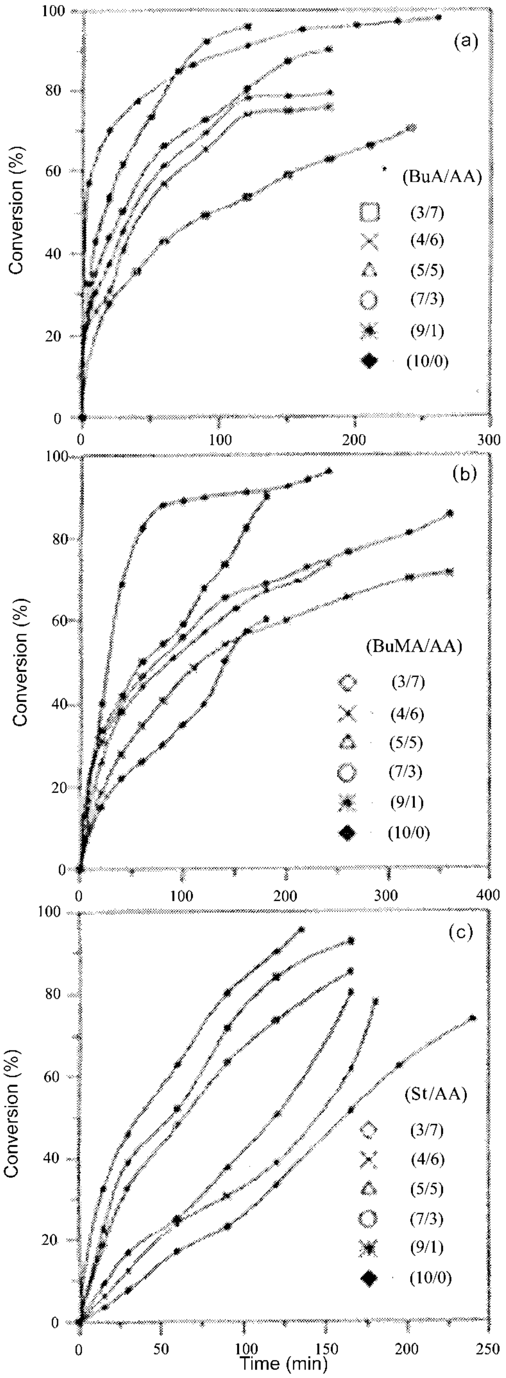


Figure 1. Conversion-time curves for the emulsion copolymerization of (a) BuA/AA, (b) (BuMA/AA) and (c) St/AA for different monomer ratios at 65°C.

The two monomers incorporated into the copolymer depending on their relative concentrations and reactivities. The ^{1}HNMR spectra for homopolymers of AA, BuA, BuMA and St are shown in Fig. 2 for comparison with their copolymers.

The composition of the obtained five copolymers was determined quantitatively by ^{1}HNMR spectrometry on the basis of the following characteristic bands illustrated in Tables 1, 3 and 5.

The molar compositions of these copolymers are given in Table 2. The molar compositions of copolymers of (series 2) are given in Table 4. The molar compositions of copolymers of (series 3) are given in Table 6.

The peak area integrations represented in Tables 2, 4 & 6 were calculated from the original NMR spectra. Some representive spectra are illustrated in Figs. 3a–c.

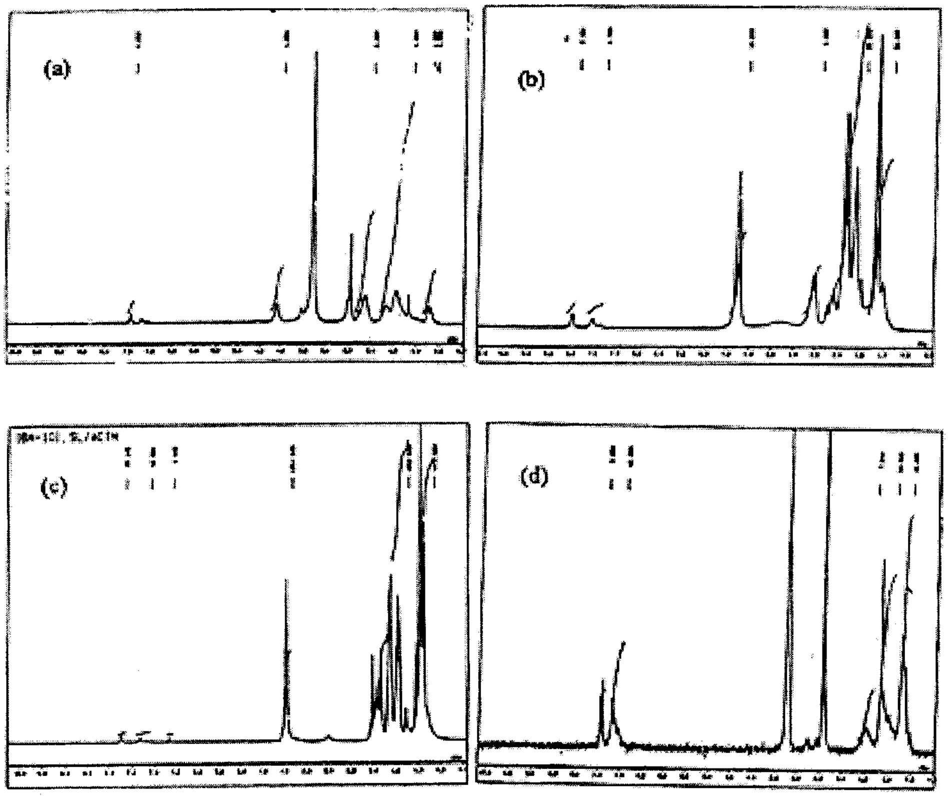
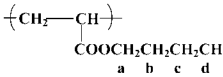
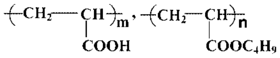


Figure 2. Proton NMR spectrum for homopolymers of (a) AA, (b) BuA, (c) BuMA, and (d) St.

Table 1. Chemical Shifts of (BuA/AA) Copolymers (Series 1)*

Resonance Signal (PPM)	Proton	Assignment
3.7–4.5	–(CH_2)– (a) (2H)	 $\left(CH_2 - \underset{COOCH_2CH_2CH_2CH_3}{CH} \right)$ a b c d
2–2.7	–(CH)– (α) (1H AA + 1H BuA)	 $\left(CH_2 - \underset{COOH}{CH} \right)_m , \left(CH_2 - \underset{COOC_4H_9}{CH} \right)_n$

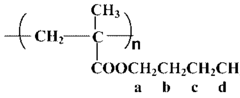
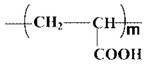
* The molar compositions of these copolymers are given in Table 2.

Table 2. Initial Monomer Concentration and Molar Composition of (BuA/AA) Copolymers (Series 1)

	Initial Concentration in the Feed (mol)		Peak Area Integration*		Copolymer Composition	
			BuA	AA	BuA	AA
Copolymer No.	M_1 (BuA)	M_2 (AA)	2H	1H	m_1	m_2
I	0.02340	0.09710	9.2930	10.3325	4.6465	10.3325
II	0.03125	0.08058	10.317	4.28450	5.1585	4.28450
III	0.03900	0.06930	7.6810	2.54150	3.8405	2.54150
IV	0.04680	0.05550	30.000	5.80000	15.000	5.80000
V	0.05468	0.04160	7.0040	0.68500	3.5020	0.68500

* Peak area integration are obtained from NMR data.

Table 3. Chemical Shifts of (BuMA/AA) Copolymers (Series 2)*

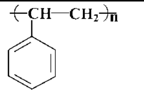
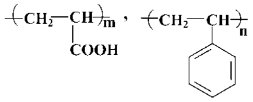
Resonance Signal (PPM)	Proton	Assignment
3.7–4.5	–(CH_2)– (a) (2H)	 $\left(CH_2 - \underset{COOCH_2CH_2CH_2CH_3}{\overset{CH_3}{C}} \right)_n$ a b c d
2–2.7	–(CH)– (α) –(1H)–	 $\left(CH_2 - \underset{COOH}{CH} \right)_m$

* The molar compositions of these copolymers are given in Table 4.

Table 4. Initial Monomer Concentration and Molar Composition of (BuMA/AA) Copolymers (Series 2)

Copolymer No.	Initial Concentration in the Feed (mol)		Peak Area Integration		Copolymer Composition	
			BuMA	AA	BuMA	AA
	M_1(BuMA)	M_2 (AA)	2H	1H	m_1	m_2
I	0.021	0.0971	8.4910	9.000	4.2455	9.000
II	0.0281	0.0832	5.8700	3.476	2.9350	3.476
III	0.0351	0.0693	17.134	9.000	8.5670	9.000
IV	0.042	0.0555	9.2870	3.755	4.6430	3.755
V	0.0492	0.0416	30.642	9.000	15.321	9.000

Table 5. Chemical Shifts of (St/AA) Copolymers (Series 3)*

Resonance Signal (PPM)	Proton	Assignment
6.0–7.5	styrene (5H)	
2.0–2.7	–(CH)– (α) (1H St + 1H AA)	

* The molar compositions of these copolymers of series 3 are given in Table 6.

Table 6. Initial Monomer Concentration and Molar Composition of (St/AA) Copolymers (Series 3)

Copolymer No.	Initial Concentration in the Feed (mol)		Peak Area Integration		Copolymer Composition	
			St	AA	St	AA
	M_1 (St)	M_2 (AA)	5H	1H	m_1	m_2
I	0.0288	0.0970	102.25	35.309	20.540	35.309
II	0.0384	0.0832	12.103	3.2260	2.4206	3.2260
III	0.0480	0.06938	9.7770	1.9740	1.9550	1.9740
IV	0.0576	0.05550	75.845	13.346	15.169	13.346
V	0.0673	0.04160	9.4870	1.2690	1.8970	1.2690

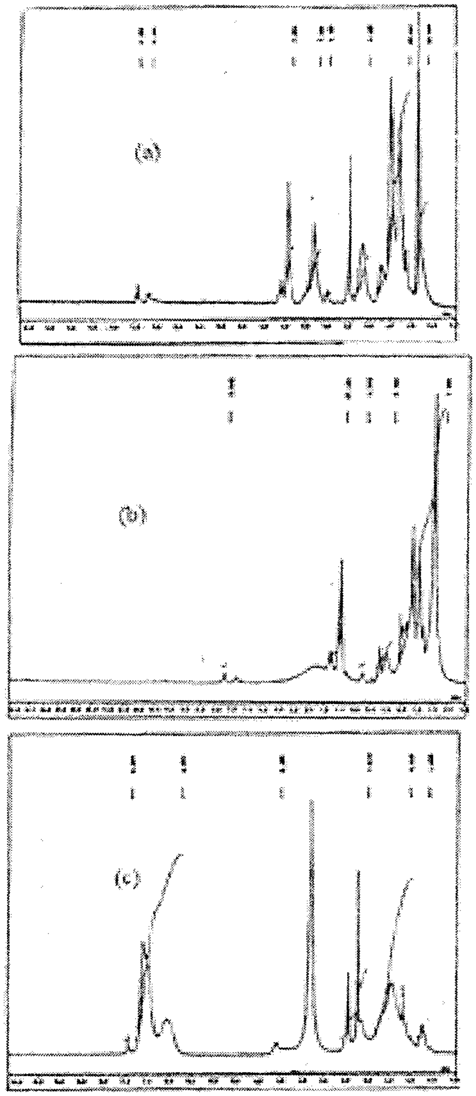


Figure 3. Proton NMR spectra for binary chelating copolymers of (a) BuA/AA (III), (b) BuMA/AA (III), and (c) St/AA (III).

Determination of the Monomer Reactivity Ratios

Fineman Ross Equation[33]

The monomer reactivity ratios r_1 and r_2 of the prepared copolymers were calculated from the data presented in Tables 2, 4 and 6 by application of the Fineman–ross equation.[33]

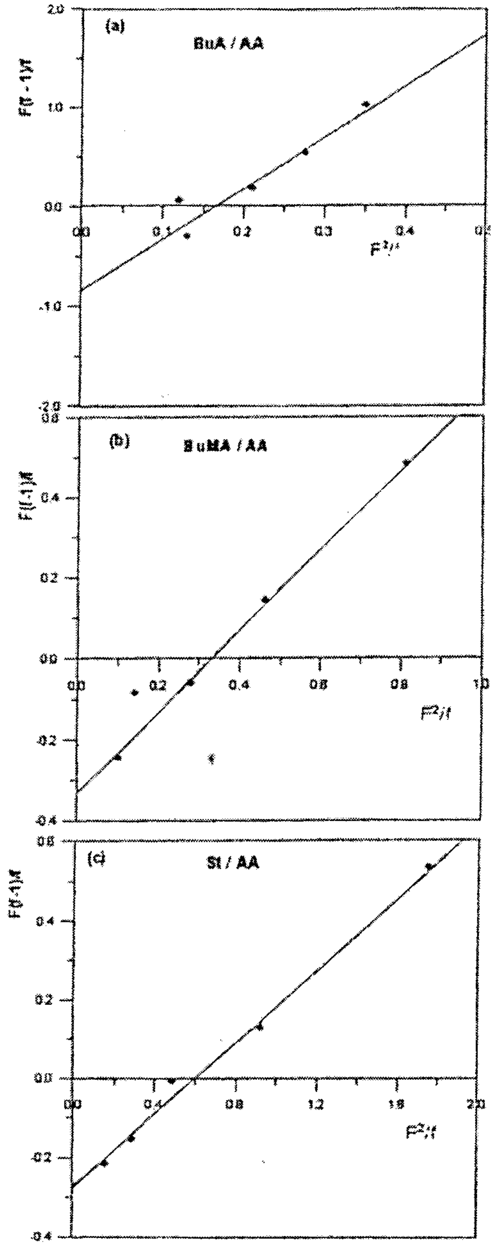


Figure 4. Determination of the reactivity ratios for the (a) BuA/AA, (b) BuMA/AA, and (c) St/AA monomers by Finneman–Ross equation.

$$\frac{F}{f}(f-1) = rl\left(\frac{F^2}{f}\right) - r_2$$

where $F = M_1/M_2$ molar ratio for monomer mixture; $f = m_1/m_2$ molar ratio for polymer composition.

In all cases, the polymer conversion was kept below (10%).

A plot of $F(f-1)/f$ vs. F^2/f gives a straight line Fig. 4. The slope and intercept of the diagram are equal to r_1 and r_2, respectively. The values of reactivity ratio for BuA/AA (series 1), BuMA/AA (series 2) and St/AA (series 3) which calculated from Fig. 4 are r_1 (BuA) = 5.625 and r_2 (AA) = 0.98 for (series 1), r_1 (BuMA) = 1.07 and r_2 (AA) = 0.33 for (series 2) and r_1 (St) = 0.5 and r_2 (AA) = 0.29 for (series 3).

On the other hand, r_1 and r_2 were determined using the data extracted from ^{1}HNMR by applying Kelen–Tüdös equation.[34]

$$\frac{a(b-1)}{\alpha\, b + a^2} = (r_1 + r^2/\alpha) \qquad \frac{a^2}{\alpha\, b + a^2} - r_2/\alpha$$

where $a = M_1/M_2$, $b = m_1\,/m_2$, $\alpha = a_{min} \times a_{max}/(b_{min} \times b_{max})^{1/2}$

Plotting $\xi = \frac{a(b-1)}{\alpha\, b+a^2}$ vs. $\eta = \frac{a^2}{\alpha\, b+a^2}$ gives a straight line as shown in Fig. 5. Table 7 illustrates monomer reactivity ratios for copolymerization of BuA/AA (series 1), BuMA/AA (series 2) and St/AA (series 3) as determined from Finemen–Ross and Kelen–Tüdös equations.

It is clear that r_1 and r_2 have the same value determined from Fineman–Ross and Kelen–Tüdös. The values of r_1 and r_2 for series 1, 2 and 3 indicate the preferential addition of BuA, BuMA and St to the growing macro radicals. From this, it is evident that the BuA/AA, BuMA/AA and St/AA copolymers consist of longer sequences of BuA, BuMA and St units interrupted by AA units.

There are some deviations in the reactivity ratios of the prepared acrylic acid comonomer than that previously mentioned in the literature due to reaction conditions (type of initiator, type of polymerization reaction, temperature, etc.,). This process can be described as a grafting process for acrylic acid monomer onto the growing BuA, BuMA and St macro radicals. These results are in agreement with the results in the literature. There are a number of articles to clarify this point of view. As an example, the radical copolymerization of acrylic acid and acrylamide at different temperatures showed different values r1 = 1.43 and r2 = 0.6 at 25°C and r1 = 0.36 and r2 = 1.38 at 60°C.[35,36] Also, the copolymerization of methyl acrylate and vinyl chloride showed that r1 = 4 and r2 = 0.06 at 45°C and r1 = 9 and r2 = 0.083 at 50°C for the same copolymer at different temperatures.[37,38] In the copolymerization of methyl-methacrylate and acrylonitrile using PhMgI in toluene, it was found that r1 = 0.02 and r2 = 4 and r1 = 0.05 and r2 = 1.3 at (−78°C and −40°C) respectively.[39]

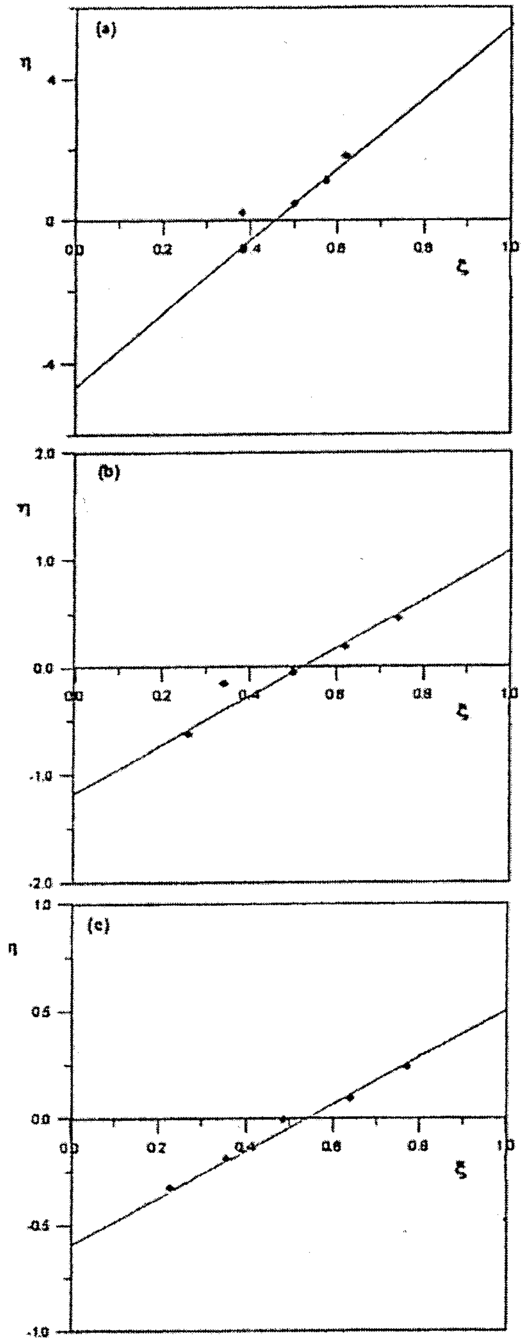


Figure 5. Determination of the reactivity ratios for the (a) BuA/AA, (b) BuMA/AA, and (c) St/AA monomers by Kelen–Tüdös equation.

Table 7. Monomer Reactivity Ratio for Copolymerization of Series (1, 2, and 3)

	Fineman–Ross		Kelen–Tüdös	
Copolymer Series	r_1	r_2	r_1	r_2
BuA/AA (1)	5.63	0.98	5.65	0.98
BuMA/AA (2)	1.07	0.33	1.15	0.34
St/AA (3)	0.50	0.29	0.52	0.28

The composition curves for the investigated systems (series 1, 2, and 3) are illustrated in Fig. 6. From Table 7 it is clear that the reactivity ratios (r_1 and r_2) for St/AA copolymer (series 3) are both less than unity, and this system should possess azeotropic composition. On the other hand, the composition curve for St/AA (series 3) illustrated in Fig. 6 cross the line representing $F_1 = f_1$ at 58%. This point of intersection corresponds to the azeotopic composition yielding homogenous copolymer regardless of conversion.

Characterization of the Copolymers of (Series 1, 2, and 3)

FT-IR Spectroscopy

Analysis of IR spectra of BuMA and St homopolymers and their copolymers (III) Figs. 7a–d gives a good information about the structure of these polymers. The characteristic bands at 1730–1770 cm^{-1} indicate the presence of C=O (i.e., the presence of carboxylic end group), 2860–2963 cm^{-1} indicate the presence of CH_2 group and the broad band at 3300–3600 cm^{-1} indicate the presence of hydroxyl of carboxylic groups of acrylic acid. The bands shifted slightly from their homopolymers due to copolymerization.

Thermo Gravimetric Analysis (TGA)

The TG curves of AA, BuMA and St homopolymers and their binary copolymer (III) are shown in Figs. 8a and 8b. From these figures, it is clearly seen that BuMA and St homopolymers show higher thermal stability than their binary copolymers with AA. This can be attributed to the less thermal stability of acrylic acid moiety due to the decarboxylation process, which occurs leading to a destruction of the polyene structures.

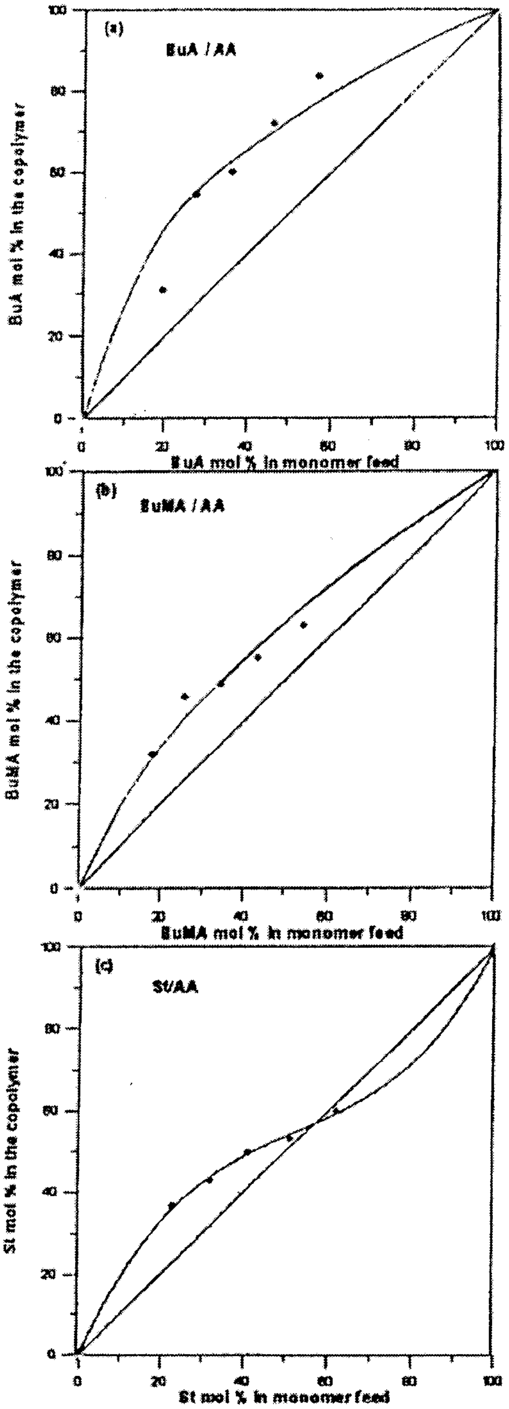


Figure 6. Comonomer-copolymer composition curves for emulsion copolymerization of (a) BuA/AA; (b) BuMA/AA, and (c) St/AA.

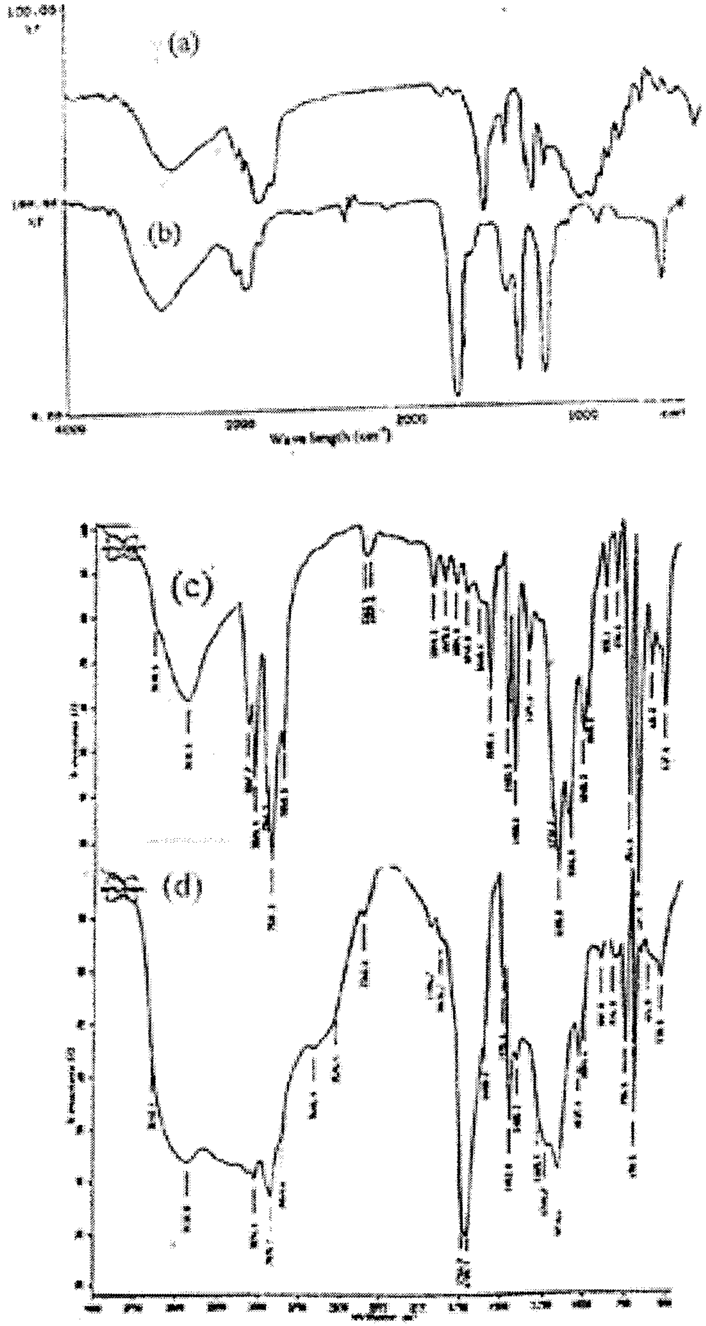


Figure 7. FT-IR spectra for the prepared polymers of (a) BuMA; (b) BuA/AA(III); (c) PSt; and (d) St/AA (III).

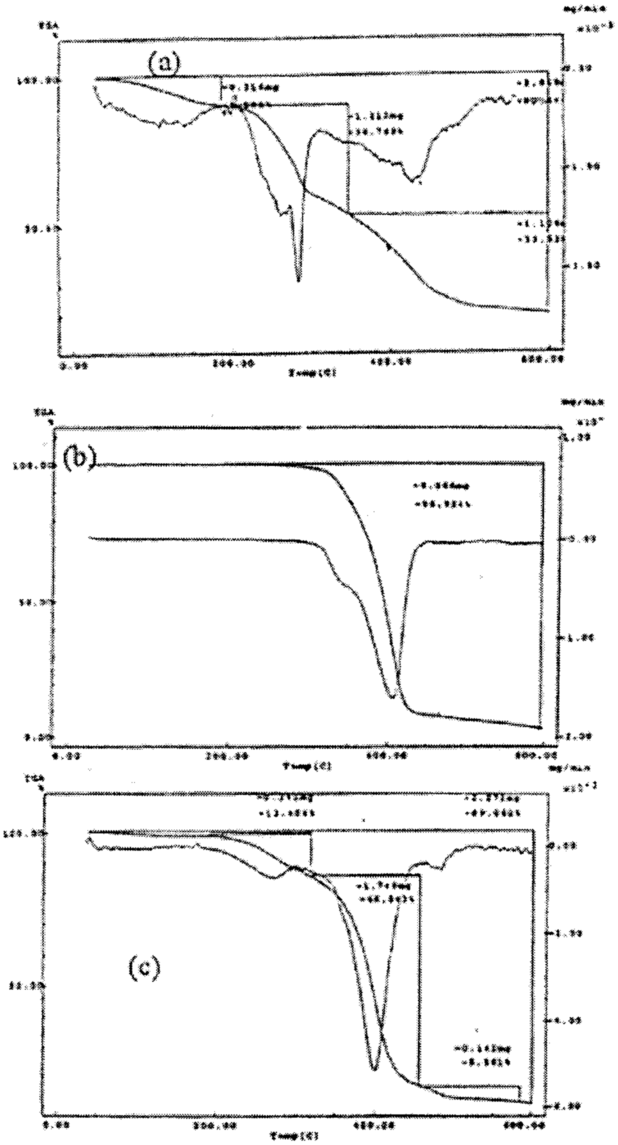


Figure 8. TGA diagram for the prepared polymers of (a) PAA; (b) PbuA; (c) BuA/AA (III); (d) St; and (e) St/AA (III).

Film Properties of the Prepared Emulsion Copolymer Latices

Film Formation

The prepared homopolymers and copolymers were casted for film formation at 70°C. The casted films were characterized. Table 8 illustrates some of these properties.

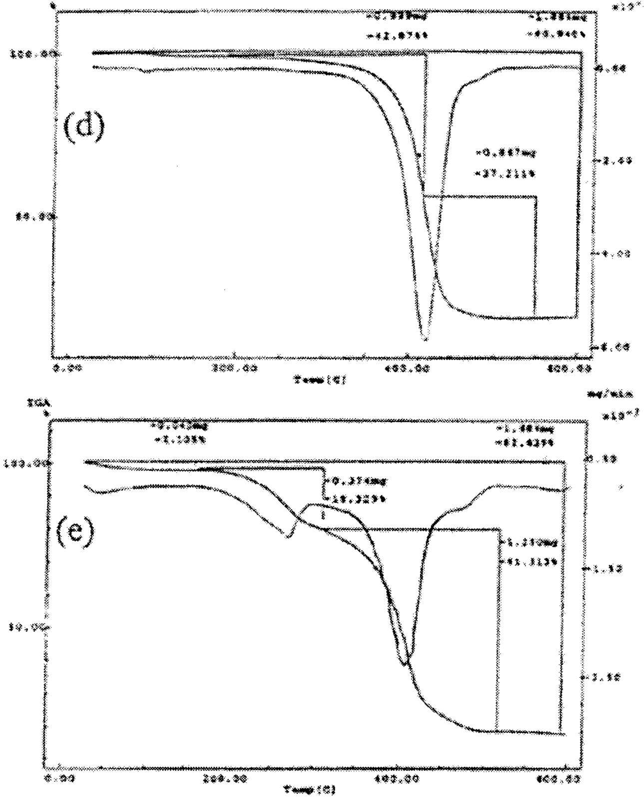


Figure 8. Continued.

Table 8. Characterization of the Prepared Polymer Films

Copolymers	Copolymer Ratio	Film Properties
PAA	–	Hard and cracked
PBuA	–	Rubbery and tacky
PBuMA	–	Rubbery and elastic
PSt	–	Hard
BuA/AA	I	Tacky
	III	//
	V	//
BuMA/AA	I	Rubbery
	III	//
	V	//
St/AA	I	Tough
	III	//
	V	//

Table 9. Physico-mechanical Properties of Butyl Methacrylate Copolymer Films

Copolymer	Copolymer Ratio	Stress at Yield, MPa	Stress at Rupture, MPa	Elongation at Yield, (%)	Elongation at Rupture, (%)
BuMA/AA	I	2.78	0.71	8.08	8.88
	III	11.7	7.12	12.28	12.56
	V	14.71	7.72	20.72	20.92

It is shown from the table that all the butyl acrylate and styrene copolymeric films are tacky and tough, respectively. Only butylmethacrylate homo and copolymeric films are rubbery in nature.

Physico-mechanical Properties of Butyl Methacrylate Copolymeric Films

The physico mechanical properties of the casted binary copolymer films of butyl methacrylate with acrylic acid for the ratios (I, III, and V) were measured and discussed. This group was chosen due to its enhanced properties. The tensile strength (stress at yield and rupture) and elongation percent at yield and at rupture were measured and calculated. The data are given in Table 9.

It is clearly seen from these results that the tensile strength and elongation at break (rupture) of the copolymer films were found to increase with increasing BuMA content in the copolymer from (17.78% to 41.65%).

Applications of Polymer Latices in Water Borne Paints

One of the most important applications for emulsion homopolymer and/or copolymer is its use in water-borne coatings. Its specialization for this purpose gained valuable interest in both research and industrial fields. This is because emulsion paints are characterized by absence of fire risk and toxic solvents; ease of application by either brush or roller; speed of drying, enabling a further coat to be applied within a few hours; finally, tools and containers can be cleaned with water.

The emulsion copolymer latices (solid content 25%) of series (1, 2, and 3) were incorporated in latex paint formulations Table 10.

To evaluate copolymer emulsions of series (1, 2, and 3) that were prepared using the redox initiation system in latex paints, the physical and mechanical characteristics of the painted films were measured and clarified. Table 11 illustrates the physical characteristics of the obtained copolymer emulsions.

Table 10. The Various Ingredients of the Latex Paint Formulations

Ingredients	Control	BuA/AA (V)	BuMA/AA (V)
Water	50	10	10
Wetting agent	0.42	0.42	0.42
Tetra potassium-pyrophosphate	0.42	0.42	0.42
Dispersing agent	0.42	0.42	0.42
Preservative	0.42	0.42	0.42
Antifoam	1.43	1.43	1.43
Ethylene glycol	4.00	4.00	4.00
The above ingredients were combined in moderate speed ball mill for fifteen minutes while stirring the mixture, the following ingredients are added:			
Micronized talc	17.32	17.32	17.32
$CaCO_3$	18.64	18.64	18.64
TiO_2 (Rutile)	44.6	44.6	44.6
The above ingredients were mixed at high speed for twenty minutes while stirring the mixture, the following ingredients are added			
Thickening agent	0.74	0.74	0.74
Antifoam	0.98	0.98	0.98
Ammonia	0.42	0.42	0.42
Mineral turpentine	0.92	0.92	0.92
The above ingredient were combined in moderate speed ball mill for fifteen minutes while stirring the mixture, the following ingredients are added:			
Styrene-acrylate emulsion (40% solid content)	60.00	–	–
Copolymer latex (25% solid content)	–	100	100

Table 11. Film Characteristics of the Various Latex Paint Formulations

Character	Control	BuA/AA (V)	BuMA/AA (V)
Drying time:			
a. Touch dry (min)	16	20	16
b. Hard dry (min)	30	41	38
Hardness (pencil)	H	2H	3H
Thickness (μ)	120	120	120
Impact resistance, Kg.m	0.6	0.6	0.6
Ductility, mm	3	2.4	2
Adhesion	Gt0	Gt1	Gt1

Gtl indicates that the cut edges are smooth and strong adhesion (90%).

Gt4 indicates that the polymer has chipped off (along the out edges) in wide steps and the chipped area is 65% or more.

Table 12. The a.c. Conductivity Measurements at Room Temperature

	a.c. Conductivity (Ω^{-1} cm^{-1})			
Copolymer	10 KHz	20 KHz	30 KHz	100 KHz
BuM/AA (III)	$10^{-6.51}$	$10^{-6.29}$	$10^{-6.19}$	$10^{-4.99}$
St/AA (III)	$10^{-6.86}$	$10^{-6.68}$	$10^{-6.6}$	$10^{-5.97}$

As shown from Table 11, it is clear that the adhesion and ductility increases with changing the type of the copolymer in the order BuA/AA > BuMA/AA.

It is clearly seen from Table 11, that the adhesion of BuA/AA is greater than that of BuMA/AA and the hardness of the painted films of BuA/AA is less than that of BuMA/AA due to the plasticizing activity of BuA than the BuMA. Finally, we can conclude that, although, acrylic latices have high hardness and low adhesion properties, BuA and BuMA are playing an important role in improving and enhancing the mechanical properties of the resulting emulsion latices due to their plasticizing nature.

Conductivity Measurements

The a.c conductivity for some of the prepared copolymers was measured at room temperature for different frequencies from (10–100 KHz). The data given in Table 12 indicate that the BuMA/AA copolymer shows higher conductivity values greater than that of St/AA copolymer having the same molar ratio in the monomer feed composition at all frequency ranges. This may be attributed to the easier mobility of the charge carriers in the former copolymer than the later due to steric hinderance effects. All mentioned copolymers show semi-conducting behavior and conductivity increases by increasing frequency.

CONCLUSIONS

Binary chelating copolymers of acrylic acid with butyl acrylate, butyl methacrylate and styrene were prepared by a semi-bath emulsion process. The prepared copolymers were characterized and the reactivity ratios of their monomers were determined. There are some deviations for the monomer reactivity ratios from that reported in literature and this is due to different reaction conditions e.g., (type of polymerization, initiator, emulsifier and temperature). The copolymers having the best physico-mechanical properties were incorporated in water-borne paints and evaluated in comparison with a commercial styrene-acrylate type emulsion as a control. The prepared binary chelating copolymers show semiconducting properties at room temperature in the range from $10^{-4.99}$ to $10^{-6.86}$ $\text{ohm}^{-1}\ \text{cm}^{-1}$.

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