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S. M. Mokhtar^a; E. M. Youssef^b; M. A. Abd El-Ghaffar^b

^a Chemistry Department, College for Women, Ain-Shams University, Cairo, Egypt ^b Department of Polymers and Pigments, National Research Center, Cairo, Egypt

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CHARACTERIZATION AND ELECTRICAL PROPERTIES OF ITACONIC ACID/BUTYLACRYLATE COPOLYMERS AND THEIR METAL COMPLEXES

S. M. Mokhtar,^{1,*} E. M. Youssef,² and M. A. Abd El-Ghaffar²

¹Chemistry Department, College for Women, Ain-Shams University, P.B. 11757, Asmaa Fahmy, St. Hellioplis, Cairo, Egypt

²Department of Polymers and Pigments, National Research Center, Dokki, Cairo, Egypt

ABSTRACT

Copolymerization of itaconic acid (IA) with butyl acrylate (BuA) has been carried out in dioxane in the presence of azobisisobutyronitrile as the initiator at 65°C. The monomer reactivity ratios (r_1 and r_2), Q and e for IA with BuA were determined and discussed. The obtained copolymers prepared by different monomer feed concentrations and their metal complexes with copper and iron salts were characterized by FTIR, UV-vis, x-ray diffraction, and thermal analysis (DSC and TG). The conductivity for the various copolymers and their metal complexes measured at room temperature showed semiconducting behavior.

Key Words: Butyl acrylate; Conductivity; Itaconic acid; Metal complexes; Reactivity ratio; Thermal analyses

INTRODUCTION

Itaconic acid (IA) was isolated in 1836 from the pyrolysis of citric acid (1). The effect of solvents on the behavior and the rate of polymerization were

*To whom correspondence should be addressed.

investigated on radical homopolymerization of itaconic acid on dioxane and ethanol at 60°C (2). Many patents in the literature describe the use of polyitaconic acid and its derivatives as rigid plastics. IA polymerizes in aqueous solution upon initiation with potassium persulfate. The effect of pH on the rate of polymerization was studied (3–5). The copolymerizations of IA with styrene, acrylonitrile, and some esters were also investigated and the monomer reactivity ratios were calculated (6–11). The terpolymerizations of IA with acrylonitrile and different types of acrylates were carried out at 70°C by a free-radical mechanism (12–15). The changes of conformation and supermolecular structure of IA with *N*-vinylpyrrolidone (NVP) and methyl methacrylate (MMA) (16) and the copolymerization of IA with styrene or butylacrylate initiated by a redox system in the presence of nonionic emulsifier have also been studied (17,18). The thermal stability and the reactivity ratios of monomethyl itaconic and itaconic anhydride with MMA were investigated (19). Characterization and physical properties of derivatives of poly (itaconic acid) (PIA) with different monomers such as acrylonitrile, styrene, and MMA were determined (20–23). In our previous studies, we have reported the complex formation of some teflon-g-acrylic acid copolymers obtained by treatment of the grafted films with metal salt solutions. The polymer metal complexes acceptable physicommechanical properties and enhanced semi-conducting behavior (23–26).

The aims of the present work are to determine the reactivity ratios of the prepared copolymer of IA and butylacrylate (BuA) and to investigate some selected properties of (IA/BuA) copolymer metal complexes and to throw light on their thermal stabilities.

EXPERIMENTAL

Materials

Itaconic acid (IA) (BDH) was used after recrystallization from distilled water, m.p. 160°C. Butylacrylate (BuA) (Aldrich) was distilled just before use. Azobisisobutyronitrile (AIBN) (Koch-Light) was recrystallized twice from methanol, m.p. 104°C. The other reagents and solvents were used after ordinary purification.

Copolymerization Procedure

Radical copolymerization was carried out in Pyrex glass ampoules charged with the required amount of the two monomers and required amount of the initiator and dioxane as solvent. The ampoules were then cooled and sealed at normal pressure. The copolymerization was carried out in a water thermostat at 65°C ($\pm 0.1^\circ\text{C}$), with periodic stirring for a definite time to always keep the conversion below 10%. At that time, the copolymerization reaction was stopped by cooling the ampoules in an ice–water–salt mixture, followed by pouring the contents into a large amount of distilled water to get rid of the formulation of any homopolymers formed. The



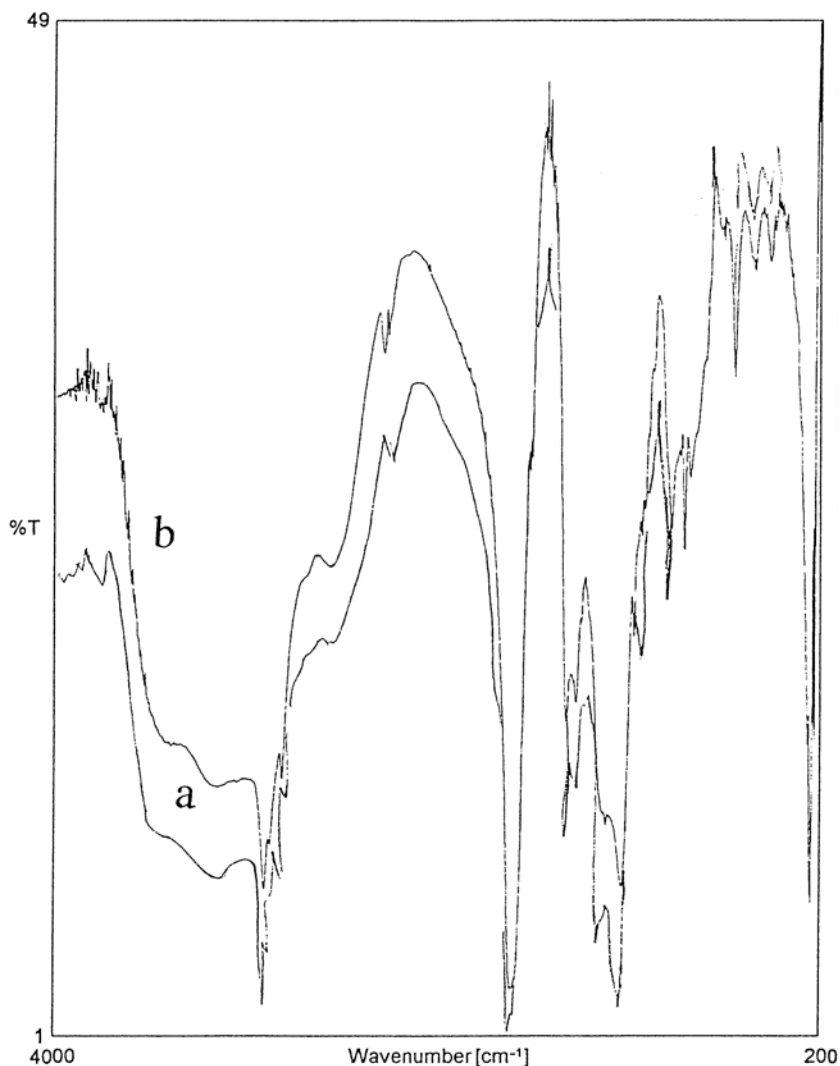


Figure 1. FTIR spectra of IA and BuA copolymers. a) IA/BuA = 30/70 mol.-%; b) IA/BuA = 60/40 mol.-%.

copolymer was purified by reprecipitation in cooled ethanol followed by ether and allowed to dry under high vacuum at room temperature.

The copolymerization analysis was calculated on the basis of the carbon content of the copolymers at the Central Micro Analytical Unit in Cairo University.

Preparation of Copolymer Metal Complexes

Copper and iron complexes of the chelating copolymer (BuA/IA) were prepared according to the following procedure: Approximately 1 g of the prepared copolymer (BuA/IA) was dissolved in 20 mL of dimethyl formamide and refluxed



Table 1. Copolymer Composition of IA/BuA in Dioxane

Monomer Composition mol.-%		Copolymer Composition mol.-%				η	ζ $\alpha = 1.147$
M ₁ (IA)	M ₂ (BuA)	C%	m ₁ (IA)	m ₂ (BuA)			
10	90	62.5	15.44	84.56	-0.409	0.055	
20	80	60.52	26.14	73.86	0.344	0.133	
30	70	58.9	34.35	65.65	-0.260	0.234	
40	60	57.58	41.23	58.77	-0.159	0.356	
50	50	56.36	47.50	52.50	-0.047	0.491	
60	40	55.15	53.74	46.26	0.068	0.628	
70	30	53.18	60.59	39.41	0.173	0.755	
80	20	52.19	68.56	31.04	0.263	0.863	
90	10	49.92	80.62	19.38	0.332	0.944	

$$\eta = G/(\alpha + f); \zeta = f/(\alpha + f); \eta = r_1\zeta - r_2/\alpha(1 - \zeta).$$

with 50 mL of 1.0 wt.-% of metal salt solution (cupric chloride or ferrous chloride) for 2 h at 100°C. The colored polymer metal complex was washed several times with distilled water, methanol, and acetone and dried in a vacuum oven at 50°C.

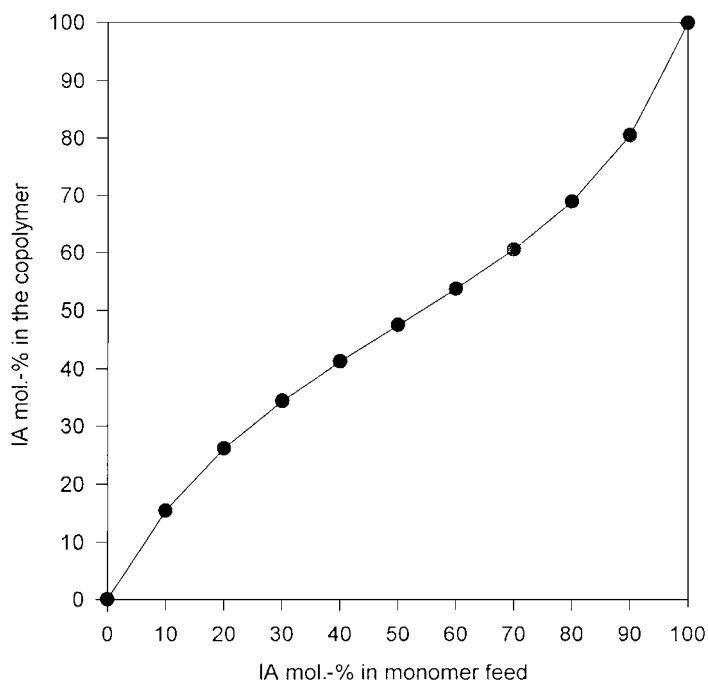


Figure 2. Comonomer-copolymer composition curves for radical copolymerization of IA and BuA in dioxane at 65°C.



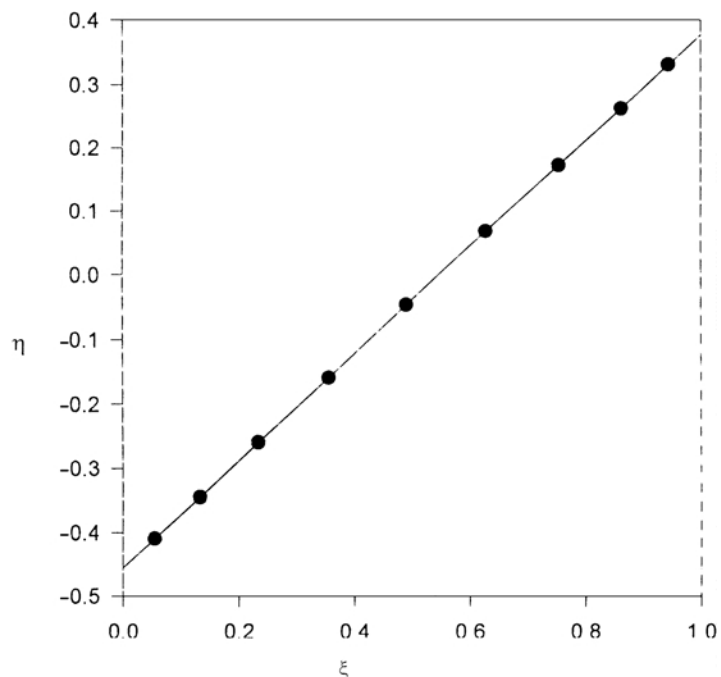


Figure 3. Kelen-Tüdös plot for the reactivity ratios of IA and BuA copolymer.

Stability Constant of the Copolymer Metal Complexes

The stability constant of the prepared complexes were determined by the continuous variation method (27) (with treating the copolymer with Cu^{+2} or Fe^{+2} in various wt.% ranging from zero to 100% in DMF. The UV-vis spectra of the complexes was recorded (the spectra of the copolymers were measured at wave length equal 276 nm in DMF using a Perkin-Elmer, Lambda 3 Spectrophotometer).

FTIR Spectroscopy

FTIR spectra was measured using a Testscan Shimadzu 8000 FTIR spectrometer.

Thermogravimetric Analysis

Thermogravimetric analysis (TG) for the various investigated samples was performed using a Shimadzu TG-50H analyzer with a heating rate of $10^\circ\text{C min}^{-1}$.



X-Ray Diffraction

The x-ray diffraction patterns were obtained using a Phillips apparatus (PW 1390 channel control and PW 1373 goniometer supply) using nickel-filtered Cu- α radiation. This technique was used to clarify the changes in morphological structure caused by complex formation.

Electrical Conductivity

Measurements of dc conductivity at room temperature were made using a specially designed cell provided with a temperature controlling system. Keithly 616 digital electrometer was used for current measurements at a certain applied voltage. Measurements were carried out using two probe electrodes.

RESULTS AND DISCUSSION

Characterization of the Copolymer of Itaconic Acid and Butyl Acrylate

Reactivity Ratios

The radical copolymerization of IA with BuA was carried out in dioxane at 65°C using 5×10^{-3} mol/L azobisisobutyronitrile (AIBN) as initiator. The FTIR

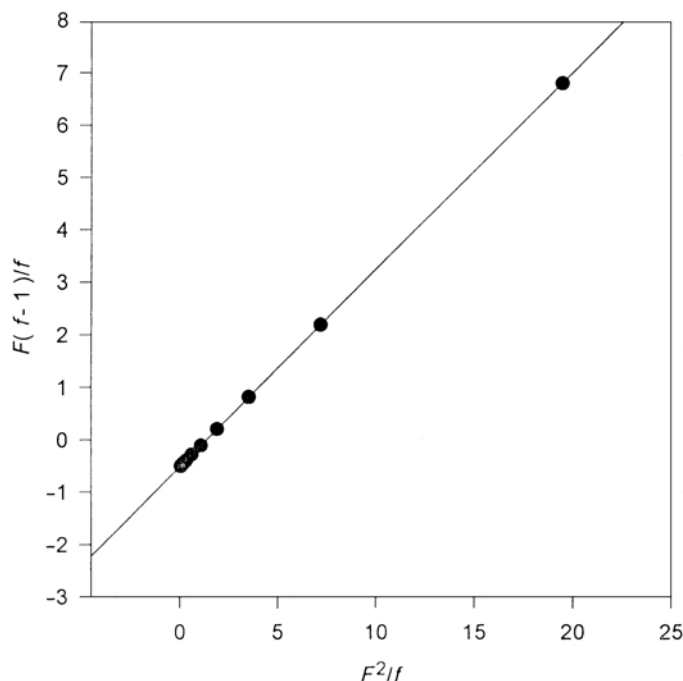


Figure 4. Determination of the reactivity ratios of IA and BuA copolymer by the Fineman-Ross equation.



Table 2. The Thermogravimetric Analyses of the Copolymer and Their Complexes

Polymer	T Initial °C	T Max °C
Pure PIA	110	360
PIA/BuA (50:50)	160	370
PIA/BuA (Cu ⁺²)	182	398
PIA/BuA (Fe ⁺²)	189	400

spectra (Fig. 1a–c) indicated the absence of the absorption band at 1640 cm⁻¹, characteristic for the carbon–carbon double bond, which indicates that true copolymer is formed, since the formation of homopolymer should be minimal due to reprecipitation of the copolymer. The composition of the monomer feed and that of the copolymers is compiled in Table 1, and the monomer–copolymer composition curves are represented in Figure 2. The reactivity ratio of IA and BuA has been calculated by Fineman-Ross (28) and Kelen-Tüdös (29). Figures 3 and 4 represent the reactivity ratios calculated by K-T and F-R methods, respectively, and it was found

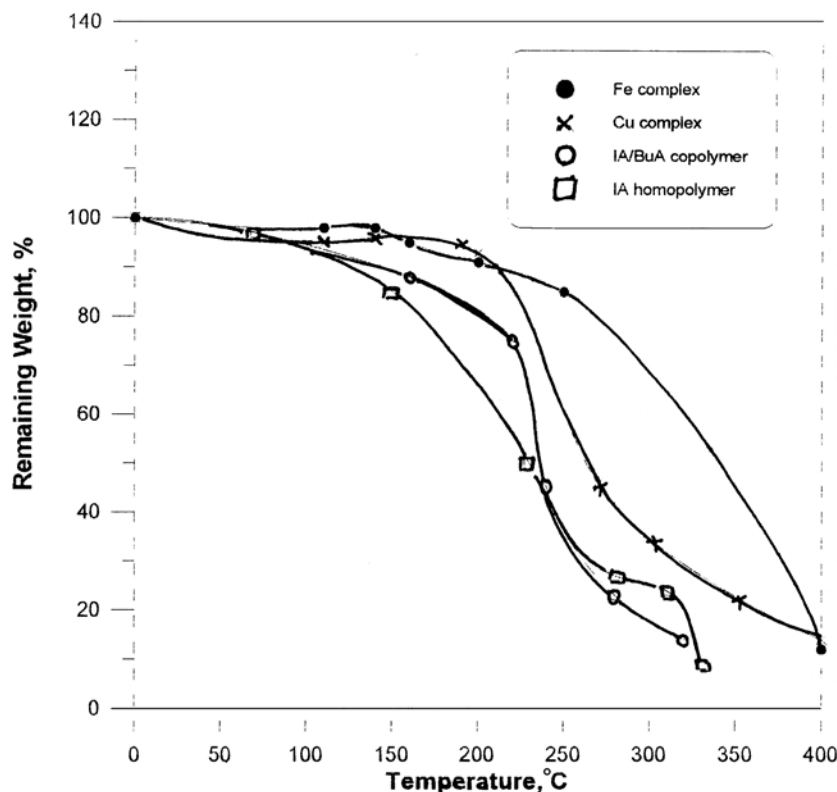


Figure 5. TG of IA and BuA copolymer and their metal complexes. MARCEL DEKKER, INC. 270 Madison Avenue, New York, New York 10016



that $r_1 = 0.377$, and $r_2 = 0.522$ for IA and BuA, respectively by the Fineman and Ross method and $r_1 = 0.38$, and $r_2 = 0.455$ by the Kelen-Tüdös method, also the values of Q_1 and e_1 were found to equal 0.148 and 0.257, respectively. Two values are usually obtained for the e parameter. The positive value was chosen because the two carboxyl groups of IA withdraw electrons from the double bond, rendering it relatively charged. It is clear from the data of r_1 and r_2 that the copolymerization of IA and BuA have an alternating tendency.

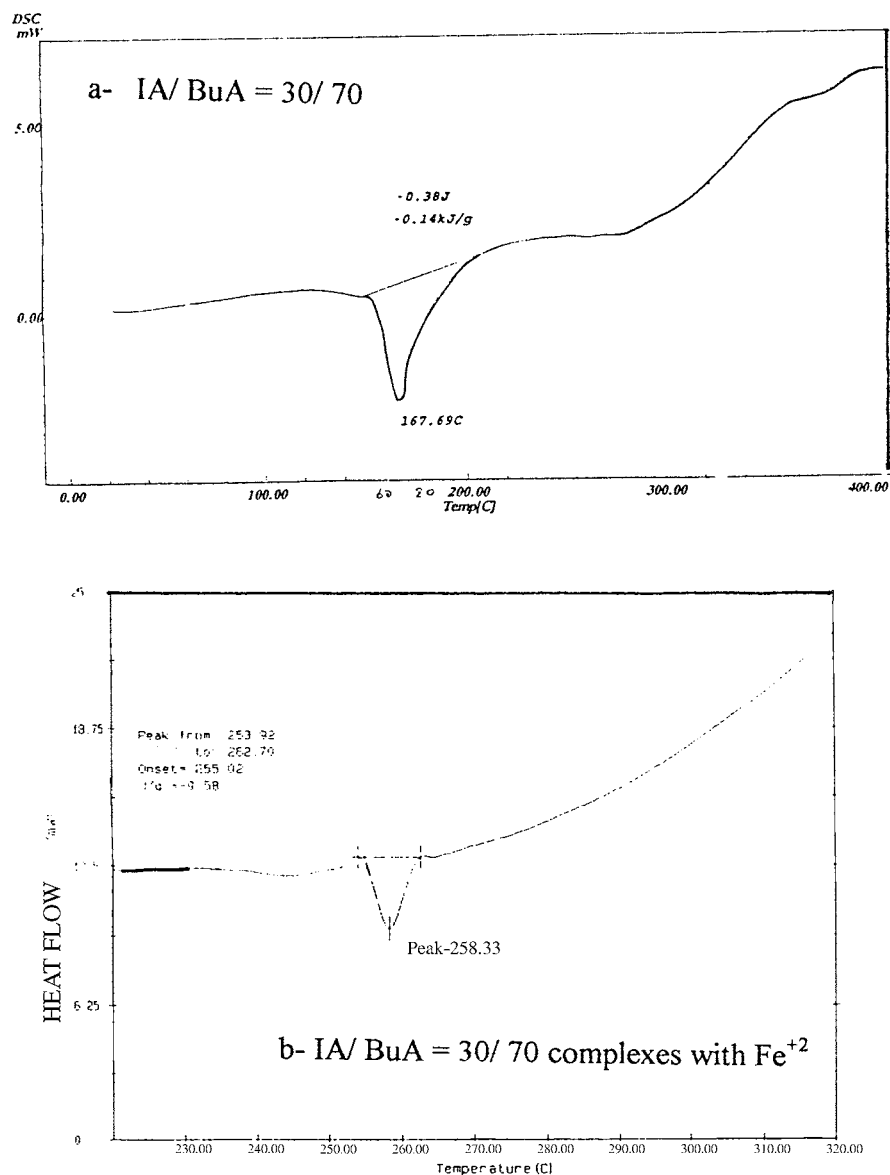


Figure 6. DSC of IA and BuA copolymer and their metal complexes.



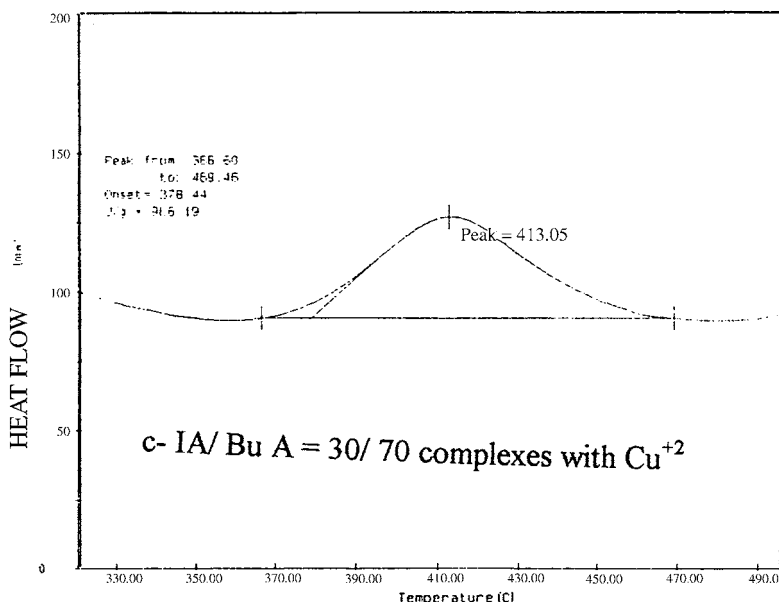


Figure 6. Continued

THERMAL ANALYSIS

The homopolymers of IA are partially decarboxylate on heating under mild conditions, because the polymers lose approximately 0.23 to 0.30 mol of CO₂ per monomer unit at 100°C. The TG curves of PIA and its copolymers with BuA, also the copolymer obtained complexed with Fe⁺² and Cu⁺², are shown in Figure 4. The remarkable weight loss (~3%) at 75°C for the polyitaconic may be attributed to the presence of a residual solvent in the polymer. The Tinit and Tmax are summarized in Table 2. Generally, the presence of BuA increases the thermal stability of PIA. Also, the thermal stability of the copolymer metal complexes are enhanced compared with the untreated copolymer because of the metal itaconic chemical bonds which strengthen the thermal stability of the polymer metal complex of itaconic acid. The IA/BuA copolymer complexed with iron gave higher thermal stability than that complexed with copper ion, this may be due to stronger a chemical bond in the case of (IA/BuA) Fe⁺² than that of (IA/BuA) Cu⁺².

Figure 6 (a–c) indicates the DSC measurement for IA and BuA copolymer (30/70) and their complexes with Fe⁺² and Cu⁺² using a Perkin-Elmer DSC7 with a scanning rate 10.0°C/min for the IA copolymer and 20.0°C/min for their copolymer complexed with the Fe⁺² and Cu⁺². The data show a single Tg value indicating random or statistical copolymers, also the reaction of Fe⁺³ and Cu⁺² with the chelating copolymer increased the glass transition temperatures of their metal complexes.



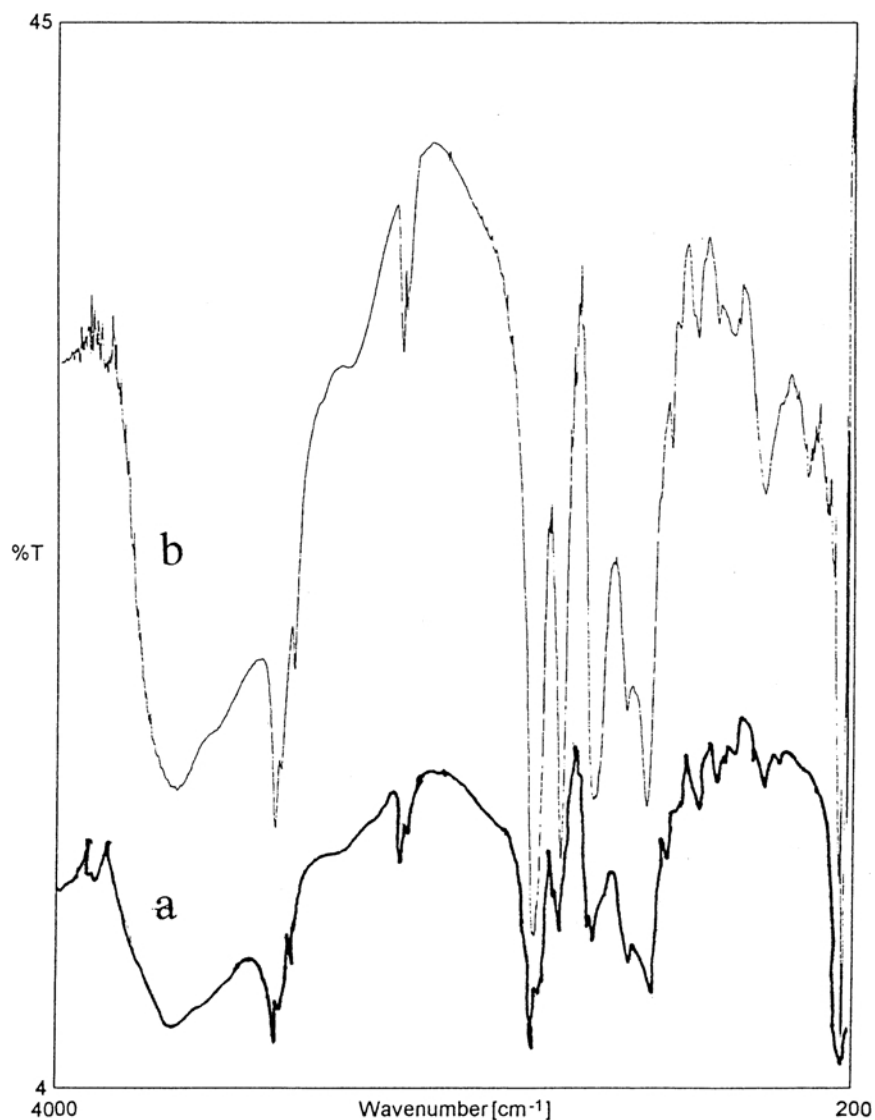


Figure 7. FTIR spectra of the copolymer complexes with Fe^{+2} . a) IA/BuA = 30/70; b) IA/BuA = 60/40.

Complexation Behavior of the Prepared Copolymers

Incorporation of a chelating moiety of the polymer chain could impart interesting property to the polymer. Polymer-metal complexes could also have catalytic activities and offer excellent models for metalloenzymes (30). The prepared copolymer showed a strong tendency for chelation (band appear at $\approx 1579 \text{ cm}^{-1}$ and 1596 cm^{-1} for the $\text{C}=\text{O}$ group with copper and iron cations, respectively, in



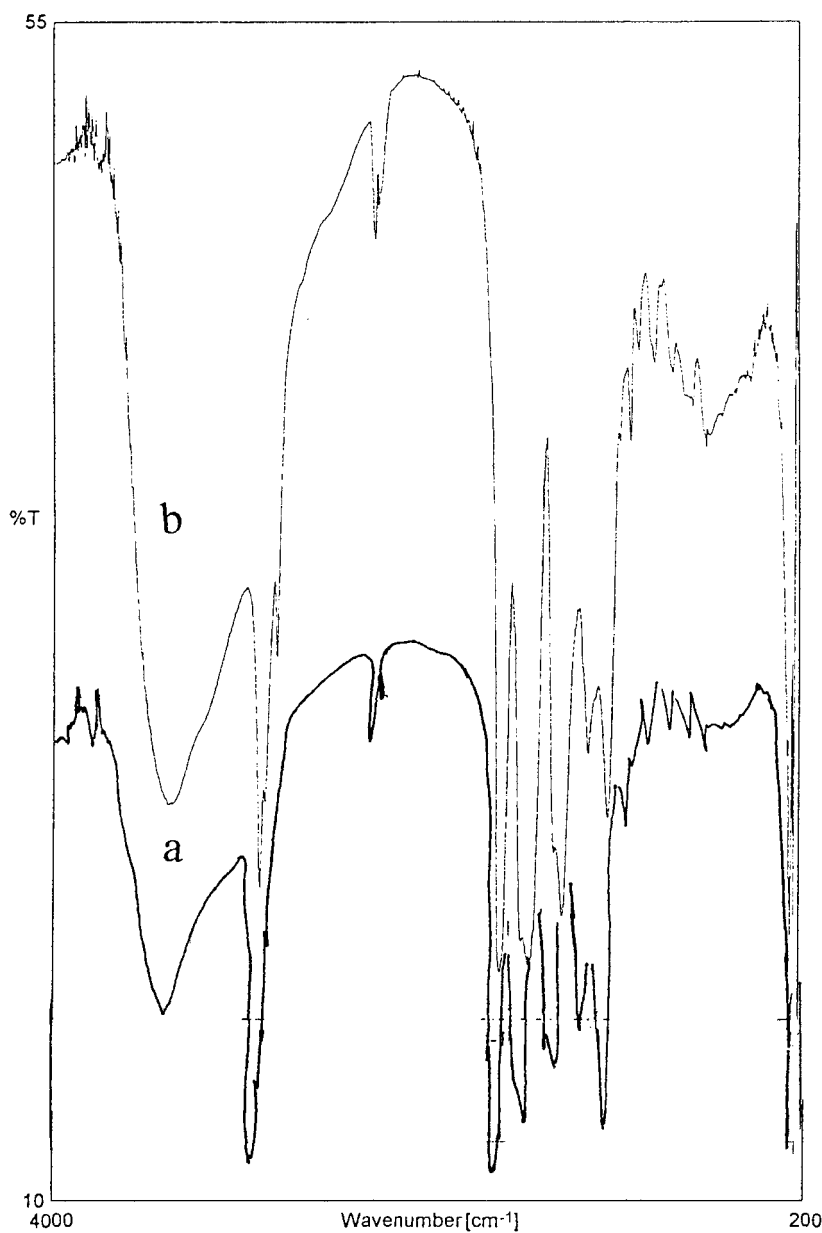


Figure 8. FTIR spectra of the copolymer complexes with Cu^{+2} . a) IA/BuA = 30/70; b) IA/BuA = 60/40.

Figures 7 and 8. The stability constant or the dissociation constants of the formed complexes were estimated by the continuous variation method (27). Table 3 indicates the values of the stability constants which are quite high indicating a strong and stable complexes between the copolymer and the cations.



Table 3. Complexation Data of Itaconic Acid and Butyl Acrylate Copolymer in DMF

IA/BuA	Metal Ion	$K^* \times 10^{-5}$	Type of Complex
30/70	Cu ⁺²	7.96	1:4
50/50	Cu ⁺²	6.235	1:4
60/40	Cu ⁺²	5.495	1:4
30/70	Fe ⁺²	2.785	1:4
50/50	Fe ⁺²	1.100	1:4
60/40	Fe ⁺²	2.105	1:4

K^* is the dissociation constant that is equal to $1/K_{stab}$.

X-Ray Diffraction Analysis

The XRD data of the (IA/BuA) copolymer and its metal complexes of Cu and Fe at the same molar ratio are given in Table 4. As shown by the data, the chelating copolymer and its metal complexes show a moderate degree of crystallinity (broad peaks) in the spectra, and there is some lack in the degree of crystallinity especially in the case of the Fe complex. There is also a characteristic change in the position of the major peaks due to metal complexation and also a change in the intensity of these peaks.

Conductivity Measurements

The conductivity of the prepared IA/BuA copolymers and their metal complexes were measured at room temperature and the data are given in Table 5. As shown from the table, it is clear that the trunk polymer and its metal complexes show semiconducting behavior, and the conductivity increases with increasing IA

Table 4. X-Ray Diffraction of the Prepared Copolymers

IA/BuA 60/40			Cu (IA/BuA) 60/40			Fe (IA/BuA) 60/40		
2θ	$d^\circ A$	I/I ₀	2θ	$d^\circ A$	I/I ₀	2θ	$d^\circ A$	I/I ₀
—	—	—	—	—	—	—	—	—
—	—	—	70.375	1.3367	29	—	—	—
—	—	—	—	—	—	—	—	—
25.498	3.4905	32	25.158	3.5369	62	—	—	—
23.798	3.7359	42	—	—	—	—	—	—
21.758	4.0813	68	—	—	—	—	—	—
—	—	—	—	4.1781	100	—	—	—
19.718	4.4986	100	21.248	—	—	—	—	—
11.219	7.8805	19	—	—	—	—	—	—
—	—	—	10.709	8.2547	41	—	—	—
5.949	14.844	32	—	—	—	—	—	—
—	—	—	—	—	—	5.609	15.743	100



Table 5. Conductivity Measurements at Room Temperature

Sample No.	(1) Blank	Cu ⁺² Complex	Fe ⁺³ Complex	Fe ⁺³ Complex
$\delta \times 10^6$	0.058	0.061	1.584	1.584
($\Omega^{-1} \text{ cm}^{-1}$)	IA/BuA (30/70)	(30/70)	(30/70)	(50/50)

content and the Fe complex has higher conductivity values greater than that of the copper one. This may be due to a chlorine atom still attached to the Fe ion.

CONCLUSION

Chelation copolymerization of itaconic acid and butylacrylate have been prepared. The reactivity ratios (r_1 and r_2) of the obtained copolymer have been calculated and showed a tendency toward alternation, also the Q and e values were determined. The FTIR and DSC measurements confirmed both the formation of true copolymerization and the complex formed between the copolymer and the metal cation. The stability constant of the prepared complexes was estimated by continuous variation method indicating that strong and stable complexes were formed. Moreover, the TG of the prepared copolymer increases with the increase of the BuA ratios in the copolymer. The conductivity measurements of the copolymer and their metal complexes showed semiconducting behavior and showed an increase with the increase of the ratio of IA.

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