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Determination of the monomer reactivity ratios for copolymerization of itaconic acid and acrylamide by conductometric titration method

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Abstract

Compositions of low conversion itaconic acid-acrylamide (IA-AAm) copolymers synthesized with solution polymerization in aqueous medium by using potassium persulfate under nitrogen atmosphere were determined by conductometric titration method. The results were evaluated by various linear and nonlinear methods. The monomer reactivity ratios were found to be $r_{IA} = 1.47 \pm 0.03$, $r_{AAm} = 0.76 \pm 0.02$ with Fineman–Ross, $r_{IA} = 1.25 \pm 0.10$, $r_{AAm} = 0.67 \pm 0.05$ with Kelen–Tüdös, $r_{IA} = 1.65 \pm 0.21$, $r_{AAm} = 0.88 \pm 0.08$ with Tidwell–Mortimer methods. For this system, the analysis of results show that IA is a more reactive monomer in IA-AAm copolymerization. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Reactivity ratio; Itaconic acid; Acrylamide

1. Introduction

Copolymerization rates and molecular weights of copolymers containing itaconic acid are higher than those obtained in homopolymerization although the synthesis of its homopolymer is difficult [1–5] while the homopolymerization and copolymerization of acrylamide have been the subject of several papers as it polymerizes easily with many vinyl monomers [6–9].

The pH during copolymerization, polymerization method and homogenity of the system have been shown to have an effect on the reactivity ratios of acrylamide and itaconic acid copolymerizations [4,10,11]. According to the results reported in the literature, tendency of both acrylamide and acidic monomer to react with acrylamide monomer increases with increasing pH [12–14].

It is known that the polyelectrolytes are ionizable compounds, which consist of at least one macromolecular ionic species and behave in a different way from neutral polymers. The dissociation behavior and quantitative determination of weak polyacids such as poly(itaconic acid), poly(maleic acid), poly(acrylic acid) and acid end groups in polyacrylamides, polyacrylonitriles initiated by various redox systems have been studied experimentally by potentiometric and conductometric titrations [15–20]. Monomer reactivity ratios for itaconic acid with most monomers have been measured in nonaqueous unbuffered solutions.

As the pH is increased, the content of the acidic component in the composition of the copolymers in aqueous polymerization systems decreases as the amount of the ionic forms is higher than the molecular ones. The aim of this work is to determine the monomer reactivity ratios of acrylamide and itaconic acid in its low conversion (<15%) copolymers, synthesized in aqueous solutions by using free radical initiator, to determine the copolymer composition by conductometric titration method.

2. Experimental

2.1. Materials

The monomers, viz., itaconic acid (IA) (Fluka) and acrylamide (AAm) (Merck) and the initiator potassium persulfate ($K_2S_2O_8$) (Merck) were used as received.

Homopolymers and copolymers of AAm and IA were synthesized in solutions prepared by distilled-deionized water using 1 mM potassium persulphate as initiator at 50°C under nitrogen atmosphere. All copolymerizations were allowed to proceed to low conversions (2–14%) by taking the polymerization period between 20 and 60 min (Table 1). Acetone is used as a precipitator to isolate the copolymers. The products were removed by filtration and dried under vacuum at room temperature.

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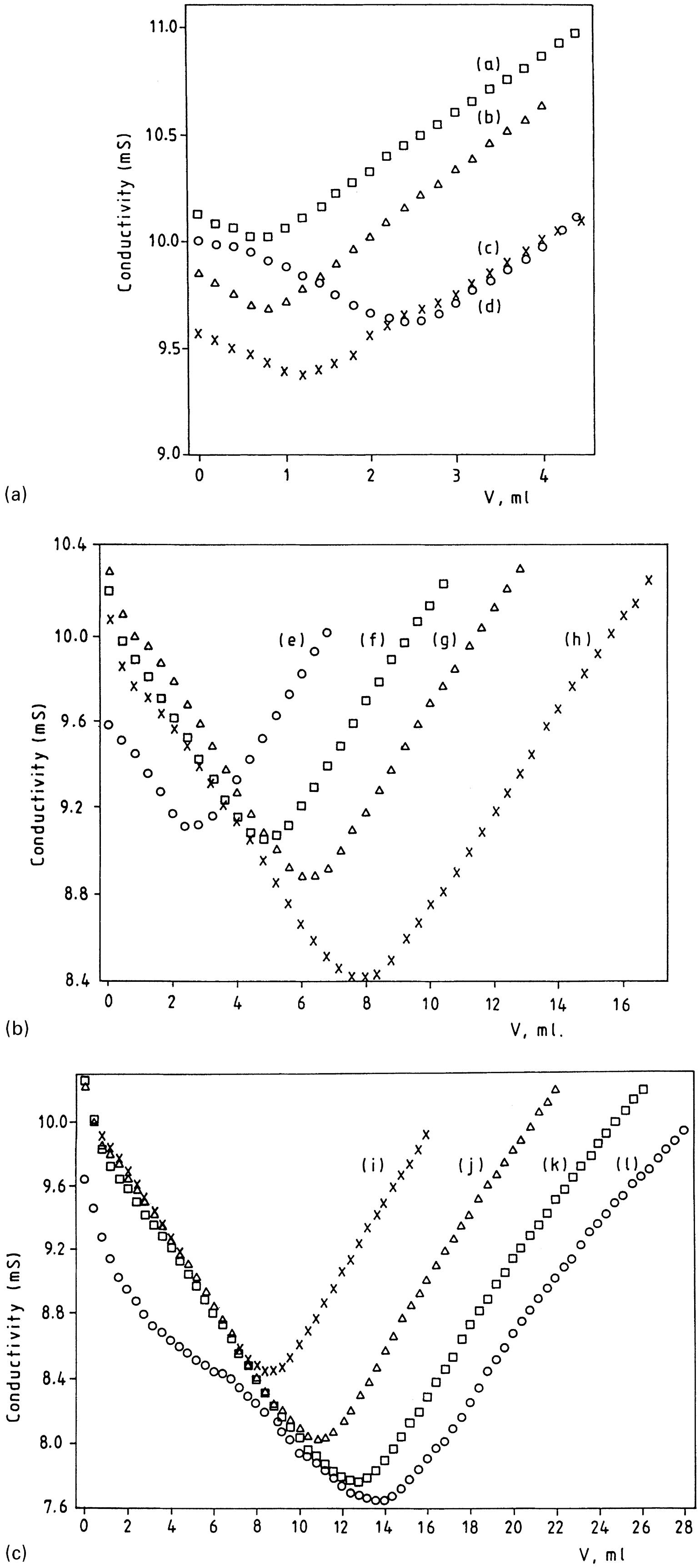

Fig. 1. (a)–(c) Conductometric titration curves of homopolymer mixtures containing PIA. (a) 2.80, (b) 3.77, (c) 5.72, (d) 10.06, (e) 12.02, (f) 26.70, (g) 35.33, (h) 52.59, (i) 56.04, (j) 75.59, (k) 91.21, and (l) 100 mol%.

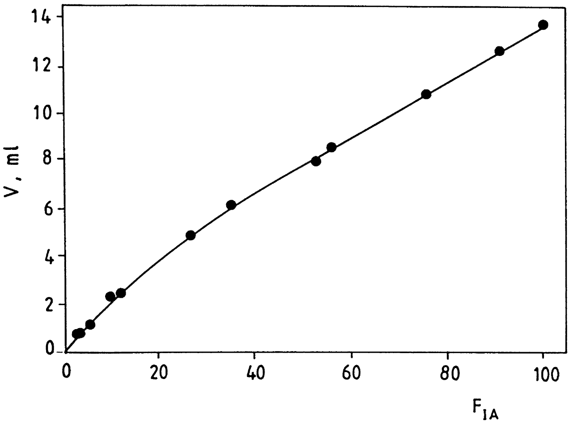

Fig. 2. Calibration curve which is used to obtain the composition of the copolymers.

2.2. Conductometric titration method

Monomer reactivity ratios of the purified polymers were determined by conductometric titration method. WTW-LF 2000 model conductometer was used for the conductivity measurements.

The conductometric titrations were carried out in a glass cell kept at constant temperature of 25°C. For each titration experiment, the cell was filled with 30 ml 0.1 N NaCl solution in which 0.1 g of solid polymer was dispersed by magnetic stirring. After the polymer completely dissolved, the solution was titrated with 0.1 N NaOH, which was added from a microburette. The conductivity values were plotted versus the milliliters of titrant. Compositions of copolymers and monomer reactivity ratios were determined from the inflection points in these titration curves.

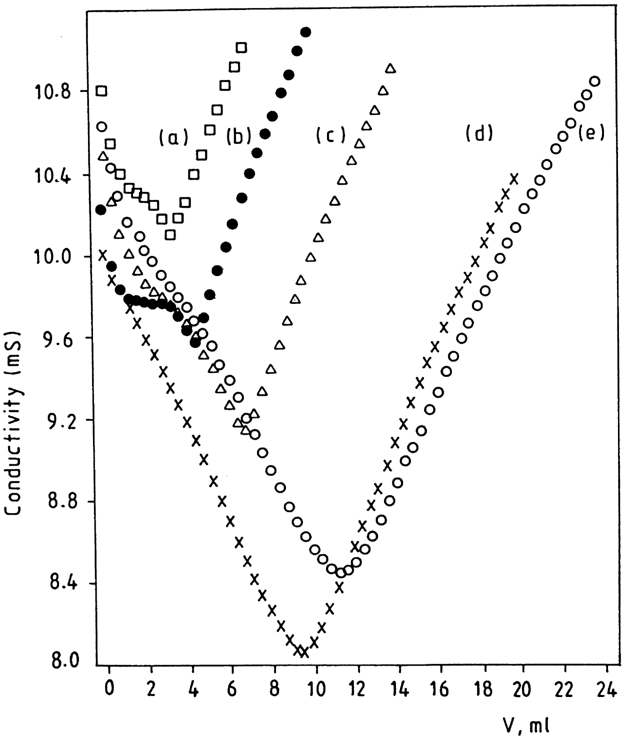

Fig. 3. Conductometric titration curves of copolymers containing IA. (a) 9.84, (b) 21.4, (c) 35.31, (d) 52.21, and (e) 73.20 mol% in the feed (f_{IA}).

Table 1
Polymerization conditions and copolymer composition data for IA-AAm copolymers

Copolymer number	Initial monomer composition of itaconic acid (f_{IA})	Conversion (%)	Copolymer composition of itaconic acid (F_{IA})
1	9.84	13.8	0.160
2	21.4	5.45	0.228
3	35.31	8.89	0.403
4	52.21	4.52	0.636
5	73.20	2.42	0.796

3. Results and discussion

3.1. Copolymer composition analysis by conductometric titration

The copolymer composition in this system involving IA which contains two carboxylic acid groups was ascertained by conductometric titration of the acidic comonomer. For this purpose, mixtures of homopolymers of PAAm and PIA were prepared with different compositions. The end points obtained from the conductometric titration curves (Fig. 1(a)–(c)) of these mixtures in aqueous solution were plotted against the contents of PIA to make a calibration curve (Fig. 2). Then the inflection points of the conductometric curves of the copolymers (Fig. 3) were placed on the reference curve to estimate the acidic comonomer content in the copolymers and the copolymer composition was found directly from this curve. The results are given in Table 1.

3.2. Monomer reactivity ratios

Several methods were applied to the experimental results to calculate the monomer reactivity ratios. The used linear analysis of the data includes Finemann–Ross [21], Kelen–Tüdös [22], extended Kelen–Tüdös [23,24] to consider the effect of conversion, and Mayo–Lewis [24,25] methods. The results are given in Table 2. The improved nonlinear least squares method of calculating copolymerization

Table 2
Results of monomer reactivity ratios calculated by using various methods

Method	r_{IA}	r_{AAm}
Finemann–Ross [21]	1.47 ± 0.03	0.76 ± 0.02
Kelen–Tüdös [22]	1.25 ± 0.10	0.67 ± 0.05
Extended Kelen–Tüdös [23,24]	1.24 ± 0.11	0.64 ± 0.05
Mayo–Lewis [24,25]	1.38 ± 0.13	0.48 ± 0.08
Tidwell–Mortimer [24,26,27]	1.65 ± 0.21	0.88 ± 0.08

reactivity ratios as outlined by Tidwell–Mortimer [24,26,27] were also applied to these data (Table 2).

Table 2 shows the discrepancies between the values obtained by the different methods used to determine the monomer reactivity ratios. The precision of experimentally determined monomer reactivity ratios depends on the experimental design and technique used to analyze the data. The nonlinear least squares analysis is a more precise method than other commonly used ones from the statistical point of view.

4. Conclusions

It is known that the amount of itaconic acid entering into the polymer depends on the pH. The extent of ionization of acidic comonomer increase and the ionizable component content in the copolymer chains decrease with an increase in the pH of the reaction mixture [4,12–14].

The samples used to calculate the reactivity ratios of IA and AAm were synthesized in aqueous solutions. The initial pH values of the polymerization solutions were in the acidic range (pH ≅ 3–5). According to our experimental results, the growing radical of IA was found to have greater affinity toward its own monomer unit because the monomer reactivity ratio for IA is greater than unity in all the methods used, either linear or nonlinear. On the contrary, the growing comonomer radical AAm also prefers to combine with IA. Consequently, we can say that both the growing radicals have a preference for the acidic monomer.

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