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Copolymerization Reactivity Ratios of Acrylic acid-Acrylonitrile, Acrylic acid-Butylacrylate, Acrylonitrile-Butylacrylate, and Terpolymerization of Arcylic acid. Acrylonitrile and Butylacrylate

by

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Copolymerization Reactivity Ratios of Acrylic acid-Acrylonitrile, Acrylic acid-Butylacrylate, Acrylonitrile-Butylacrylate, and Terpolymerization of Acrylic acid, Acrylonitrile and Butylacrylate

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Monomer reactivity ratios were determined for the copolymerization of acrylic acid, acrylonitrile and butylacrylate. To prevent the fractionation of the polymers during isolation and purification by precipitation, the unreacted monomers were removed from the mixture by evaporation in vacuo.

Using the determined reactivity ratios, the composition of three component systems of acrylic acid, acrylonitrile and butylacrylate was calculated. The predicted and experimentally observed terpolymer compositions for a given feed agree to within the experimental error.

INTRODUCTION

The studies of copolymerization were mainly concerned with the determination of the relative reactivity ratios of monomers. Relative monomer reactivity ratios have been shown to be largely independent of process or medium [1,2,3,4,5,6]. Probably the greatest source of error in calculating reactivity ratios is in the isolation and purification of the copolymer and in the determination of its composition. With appropriate corrections however values can be obtained of the probable analytical errors in the copolymer compositions.

In the isolation of the copolymer, the usual procedure is to precipitate the copolymer with a nonsolvent. Here it is first necessary to test different liquids to find the proper solvent,

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in which both monomers are soluble but in which the copolymer is insoluble. In some cases to find the proper solvent presents difficulties. To purify the copolymer the precipitation process is usually repeated at least three times.

In this paper, to prevent fractionation which might occur during the isolation and purification of the copolymer by precipitation, the copolymer has been separated from the original mixture as a film by evaporation under vacuo in an atmosphere of nitrogen. To prevent further polymerization of unreacted monomers during their removal by evaporation under vacuo an inhibitor has been used.

RESULTS AND DISCUSSION

Copolymerizations were carried out in acetone at 56 °C in such a way that low levels of conversion were obtained with each of the feed ratios. The unreacted monomers and solvent were removed by evaporation in vacuo at 40 °C. To purify the copolymer, the evaporation process was carried out at least three times. To prevent further polymerization of the unreacted monomers during evaporation thiodiphenylamine has been used as an inhibitor.

To check whether the unreacted monomers polymerised further when the inhibitor was present during the evaporation, a blank test was carried out. Acetone and initiator were heated under a reflux condenser for about two hours under the same conditions as those used for the main experiments. The solution was then cooled and divided into two equal parts. To one part an exactly known quantity of inhibitor and to the other inhibitor and acrylic acid were added. After the solvent and acrylic acid were evaporated the residues obtained had exactly the same weight. This result indicates clearly that in the presence of an inhibitor the solvent and the unreacted monomers can be removed from the copolymerization mixture by evaporation under vacuo without further polymerization taking place.

The copolymers obtained were weighed with accuracy and analysed at least twice, analyses of copolymers from a given feed were averaged.

The compositions of the copolymers obtained from the copolymerization of acrylic acid and butylacrylate were calculated from their acrylic acid contents by the titration of an ethyl alcoholic solution of the polymer with n/10 KOH and phenolphthalein. It was possible to add enough water to obtain a sharp end point, at pH 9 to 10 without precipitating the copolymer.

The compositions of the copolymers acrylonitrile - acrylic acid and acrylonitrile - butylacrylate were calculated from their nitrogen contents which were determined by the Kjeldahl method. No correction was needed for the Kjeldahl method, because the theoretical yield of nitrogen was recovered from polyacrylonitrile and it was only necessary to allow for the nitrogen present in the inhibitor (thiodiphenylamine).

The Finemann and Ross procedure [7] was used in the determination of the monomer reactivity ratios and the least squares method was used to determine the best straight line fitting the data. The slope and the negative intercept of this line gave respectively r_1 and r_2.

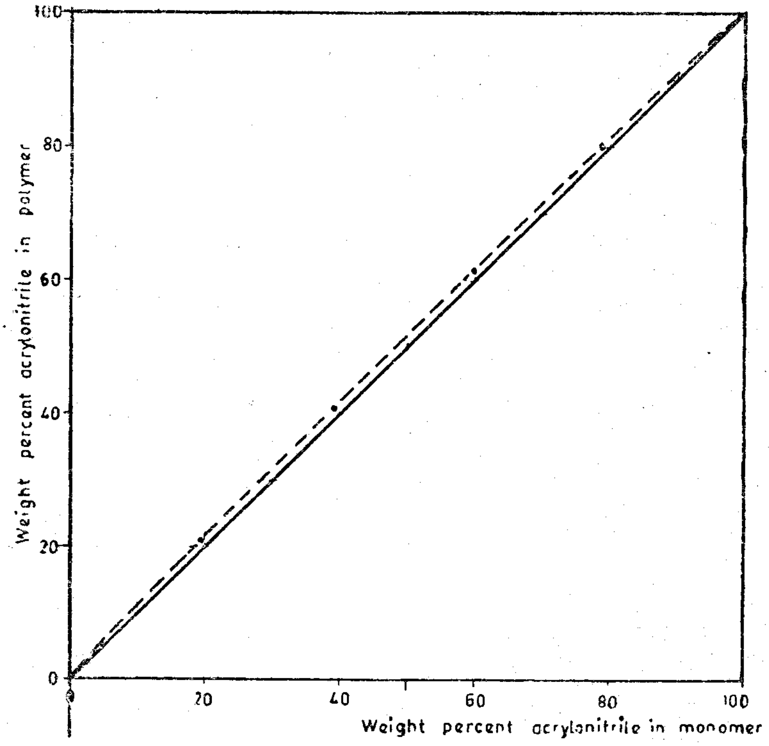
Table I lists the monomer and polymer compositions. The copolymer composition curves are shown in Fig 1 and Fig 2. A graphical representation of the Finemann and Ross parameters for the copolymerizations are shown in Fig 3.

The monomer reactivity ratios found for the copolymerization of acrylic acid, acrylonitrile and butylacrylate as weell as the previously reported results are listed in table II. As can be seen from the table there is good agreement with values for acrylonitrile and butylacrylate. However there is a difference in the values of r_1 and r_2 for the system acrylic acid and acrylonitrile.

Terpolymerization

The composition of a terpolymer formed from a monomer mixture of known composition can be calculated from the equations developed by Alfrey and Goldfinger [16] if the reactivity ratios are known for the three two-component systems.

Nine terpolymers were prepared by polymerizing the nine feed mixtures. Compositions of the terpolymers obtained experimentally and the compositions computed from the Alfrey-Goldfinger equation were compared. For calculations of the terpolymer compositions the reactivity ratios used were determined from the copolymerization experiments under the same conditions as the terpolymerization experiments.



Fig—1 Copolymer composition curve of acrylonitrile with butylacrylate

Good agreement was found between experimental results and theoretical prediction.Table III gives the composition of the monomer mixtures and the calculated and experimental composition of the terpolymers.

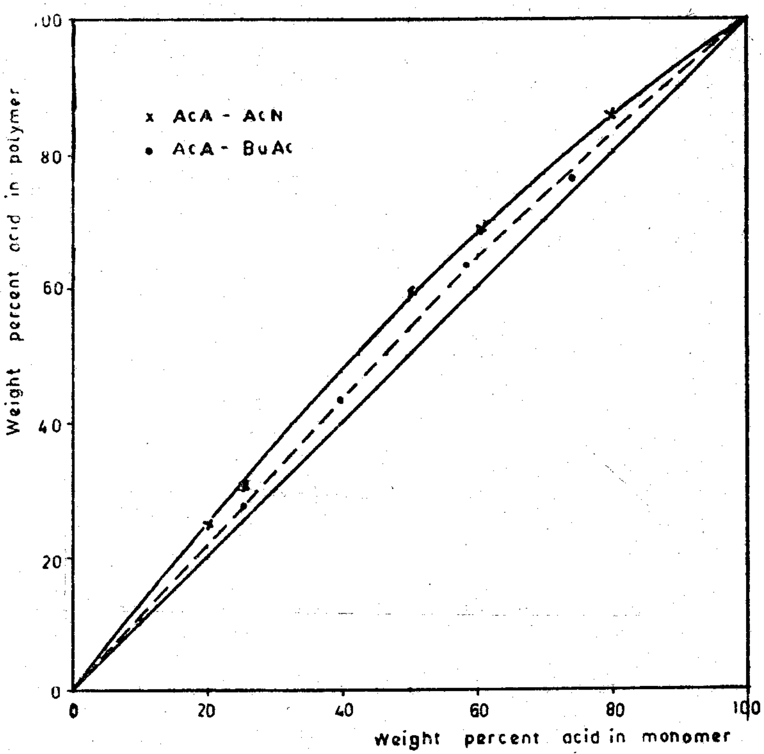


Fig-2 Copolymer compositions curves

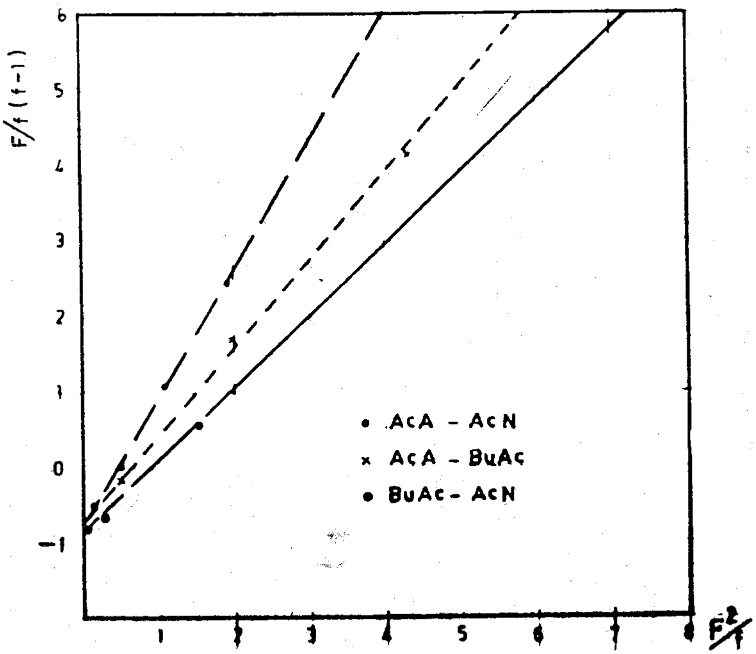


Fig 3. Copolymerization of acrylic acid, acrylonitrile and butylacrylate.

TABLE I. Monomer and Polymer Compositions and Reactivity Ratios.

Acrylic Acid (1) and Acrylonitrile (2)

Percent acid			
Monomer	Polymer	r_1	r_2
20.10	25.44	1.69 ± 0.01	0.79 ± 0.04
25.29	30.40		
50.49	59.53		
60.78	69.75		
70.25	78.78		
80.69	86.80		

Acrylic Acid (1) and Butylacrylate (2)

Percent acid			
Monomer	Polymer	r_1	r_2
25.17	28.04	1.15 ± 0.02	0.78 ± 0.09
39.95	43.71		
58.51	64.00		
73.83	76.52		

Butylacrylate (2) and Acrylonitrile (1)

Percent Butylacrylate			
Monomer	Polymer	r_1	r_2
19.89	21.06	0.92 ± 0.01	1.00 ± 0.03
40.31	40.99		
60.02	61.07		
79.74	79.93		

TABLE II. Monomer Reactivity Ratios

Acrylic Acid (1) and Acrylonitrile (2).

Present work		Literature values		
r_1	r_2	r_1	r_2	
1.69 ± 0.01	0.79 ± 0.04	1.15	0.35	[8]
		6.0 ± 2.0	0.13 ± 0.02	[9]

Acrylonitrile (1) and Butylacrylate (2)

r_1	r_2	r_1	r_2	
0.92 ± 0.01	1.00 ± 0.03	1.2 ± 0.1	0.89 ± 0.08	[10]
		1.52 ± 0.03	0.75 ± 0.18	[11]
		1.003 ± 0.012	1.005 ± 0.005	[12]
		1.0 ± 0.1	1.2 ± 0.1	[13]
		1.0 ± 0.1	0.9 ± 0.1	[14]

Acrylic Acid (1) and Butylacrylate (2)

r_1	r_2	r_1	r_2	
1.15 ± 0.02	0.78 ± 0.09	0.58	1.07	[15]

TABLE III. Three Component Polymerization of Acrylic Acid, Acrylonitrile and Butylacrylate.

Exp No:		Feed Mole %	Polymer Analysis weight %	Polymer Found	Mole % Calcd.
1	Ac A	34.32	38.54	40.98	41.22
	Ac N	46.20	26.33	38.02	38.93
	Bu Ac	19.48		21.00	19.85
2	Ac A	19.50	25.09	24.39	24.24
	Ac N	64.59	44.82	59.17	58.97
	Bu Ac	15.91		16.44	16.79
3	Ac A	25.21	24.50	30.60	30.10
	Ac N	33.10	16.49	27.97	28.62
	Bu Ac	41.69		41.43	41.29
4	Ac A	61.63	69.59	70.02	69.37
	Ac N	27.33	15.96	21.81	19.97
	Bu Ac	11.04		8.17	10.66
5	Ac A	39.10	39.43	46.12	45.55
	Ac N	30.35	15.08	23.96	24.55
	Bu Ac	30.55		29.92	29.91
6	Ac A	19.65	17.14	24.06	23.53
	Ac N	20.26	9.44	18.00	17.89
	Bu Ac	60.08		57.94	58.58
7	Ac A	8.13	14.12	11.48	10.32
	Ac N	87.15	76.16	84.08	84.55
	Bu Ac	4.72		4.44	5.13
8	Ac A	15.33	16.22	18.73	18.81
	Ac N	50.39	29.23	45.85	46.13
	Bu Ac	34.28		35.42	35.06
9	Ac A	31.25	33.95	36.79	37.54
	Ac N	44.65	26.64	39.20	38.02
	Bu Ac	24.10		24.01	24.44

EXPERIMENTAL

Copolymerization was conducted in acetone at 56 °C. 20 g of the monomer were weighed with analytical precision into a glass stoppered flask and washed quickly with 50 ml of acetone into a flask equipped with a reflux condenser which was connected to a washing flask containing liquid paraffin and fitted with a mechanical strirrer. The mixture was stirred for half an hour under a nitrogen atmosphere so as to remove oxygen. 0.02 g of Azobisisobutyronitrile was then added (0.1 percent of the total weight of the monomers) and the mixture was heated in a water bath so that its temperature was maintained at 56.0 ± 0.1 °C. After a proper conversion had been obtained (5-8 %) the flask was removed from the water bath and cooled in an ice bath. 0.02 g of Inhibitor (thiodiphenylamine) were accurately weighed and added to the mixture. The copolymers were purified by evaporation of the unreacted monomers under reduced pressure at 40°C.To remove the monomers completely the evaporation process was repeated at least three times using fresh acetone. The final residue was dissolved in acetone, transferred to a Petri dish and dried to a constant weight in a vacuum oven at 60 °C under a nitrogen atmosphere. This film of polymer obtained was weighed accurately.

Blank test: The same amount of acetone and initiator was heated under the same conditions as those used in the main experiments, and was then cooled. The solution was divided into two equal parts. An exactly known amount of inhibitor was added to one of the parts, and inhibitor and acrylic acid were added to the other. The amounts of the residue obtained from both the solutions after evaporation in vacuo were the same.

Terpolymerization was carried out under similar conditions to those used in copolymerization.

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ÖZET

Akrilik asit-akrilonitril, akrilonitril-butilakrilat, akrilik asit-butilakrilat sistemleri için kopolimerizasyon etkileşme oranları tayin edilmiştir. Polimerlerin, izolasyonu ve saflandırılması esnasında fraksiyonlara ayrılmasına mani olmak üzere reaksiyona girmeyen monomerler ve çözücü vakumda buharlaştırılarak uzaklaştırılmıştır.

Tayin edilen "etkileşme oranlarını" kullanmak sureti ile akrilik asit-akrilonitril-butil akrilat terpolimerinin muhtelif monomer konsantrasyonuna karşı bileşimleri hesaplanmış ve elde edilen neticeler deneylerle bulunanlar ile karşılaştırılmış ve değerlerin yakın olduğu tesbit edilmiştir.

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