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On the preparation of acrylic acid/vinyl acetate copolymers with constant composition — 1. Copolymerization reactivity ratios

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In the present work, low conversion acrylic acid (AA)/vinyl acetate (VAc) copolymerizations were carried out in azeotropic ethanol/water solutions containing 93% in weight of ethanol. Reactivity ratios were determined by several methods and shown to be equal to $r_{AA} = 2.6$ and $r_{VAc} = 0.04$. © 1997 Elsevier Science Ltd.

(Keywords: reactivity ratio; acrylic acid; vinyl acetate)

Introduction

Acrylic acid (AA) and vinyl acetate (VAc) monomers present very different reactivity ratios. Copolymers produced in bulk and solution copolymerization do not present homogeneous chemical composition owing to the preferential polymerization of the more active monomer species, which is acrylic acid.

Bourdais [1] carried out the copolymerization of AA and VAc in benzene. He studied the influence of pH on the reactivity and observed that the ionization does not modify the reactivity of the acid. Furthermore, he reported values of $r_{AA} = 10$ and $r_{VAc} = 0.01$.

However, it is possible to decrease the chemical heterogeneity by using a solvent that is capable of interacting with the monomers and decreasing the reactivity ratios [2]. Nesterova et al. [3] copolymerized both monomers in ethanol and ethanol/water solutions and observed that the copolymerization in ethanol decreases the composition of AA in the copolymer and that this effect is increased in presence of water. The effects of the water and other solvents on the AA/VAc copolymerization in methanol and methanol/water solution have been studied [4,5].

Ethanol/water solution at 93/7 w/w is an adequate solvent for AA/VAc polymerizations because they dissolve both poly(acrylic acid), poly(vinyl acetate) and poly(acrylic acid-co-vinyl acetate) polymers. Besides, these solutions may be obtained by distillation as an azeotrope. The aim of this work is to determine the monomer reactivity ratios in the AA/VAc polymerization in azeotropic ethanol/water solutions (93/7 w/w) and compare the results obtained with those reported by Nesterova et al. [3].

Experimental part

The AA monomer was distilled at reduced pressure. During distillation the stillpot contained an inhibitor (BHT) and the column and condenser were packed with copper helixes. The VAc monomer was distilled at normal pressure. The two monomers were stored at low temperature.

The copolymers containing different molar ratios of AA in the feed were prepared by polymerization in ethanol/water solutions (93/7 w/w) at 75°C using 0.7% (w/w) benzoyl peroxide as the initiator. Copolymerization was carried out in solutions containing 70% in volume of solvent and 30% in volume of the AA/VAc comonomer mixture, so that the initial AA concentration ranged from 0.03 to 1.75 mol l^{-1}. Monomer mixtures were prepared gravimetrically before mixing with the solvent. The reaction was carried out in a round bottom flask with condenser. The reaction mixture was bubbled using an inert gas and at the same time it was cooled. Later the polymerization was carried out during the time required to obtain conversions below 7%. Copolymers were purified in order to eliminate the solvent, the remainders of initiator and the residual monomers. Monomer conversion was evaluated gravimetrically during copolymer purification, by drying the polymer mass in vacuum ovens at ambient temperature, after precipitation in water (vinyl acetate rich polymers) or ethyl acetate (acrylic acid rich polymers) and centrifugation. Centrifugations were carried out for 10–15 min at 5000 rev min^{-1} with a Janetzki centrifuge. The final dried copolymer was used to determine the copolymer composition. Copolymer compositions of AA and VAc were determined by potentiometric titration in solutions of 0.05 M NaCl in order to improve the detection of the inflection point in the curve [6].

The concentration of ethanol in the azeotropic solution was checked by gas chromatography, refraction index measurements and density measurements, so that azeotropic composition may be guaranteed.

The reactivity ratio values were evaluated with a computer program [7] developed in our laboratory.

Results and discussion

Table 1 shows the monomer mole fraction in the feed and in respective copolymers obtained for the different experiments performed. Monomer conversions were always kept below 7%.

Copolymerization composition data were used to calculate reactivity ratios according to the terminal model. Values of r_{AA} and r_{VAc} were estimated using the following methods: Kelen–Tüdös [8], Tidwell–Mortimer [9], Fineman–Ross [10] and Mayo–Lewis [11].

Table 2 shows that there are some discrepancies between the values obtained by the different methods used to determine the reactivity ratios. Various researchers have

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Table 1 Copolymer composition data for AA and VAc copolymers

Sample	f_{AA}	F_{AA}	Conversion (%)
1	0.0089	0.13	7.0
2	0.0353	0.34	6.3
3	0.0353	0.35	4.1
4	0.0353	0.34	6.2
5	0.0614	0.42	4.2
6	0.0639	0.42	3.7
7	0.1041	0.50	6.3
8	0.1705	0.56	5.8
9	0.2504	0.61	3.7
10	0.3043	0.68	7.0
11	0.4711	0.73	7.0

f_{AA} mol fraction of acrylic acid in the monomer feed. F_{AA} mol fraction of acrylic acid in copolymer.

Table 2 Reactivity ratios for AA and VAc obtained according to different methods

Method	r_{AA}	r_{VAc}
Mayo–Lewis	1.4 ± 0.3	0.039 ± 0.001
Fineman–Ross[a]	2.2 ± 0.2	0.03 ± 0.02
Tidwell–Mortimer	2.5 ± 0.5	0.04 ± 0.01
Kelen–Tüdös	2.6 ± 0.5	0.04 ± 0.01

[a]Acrylic acid is monomer 1.

Table 3 Reactivity ratios obtained in different solvents

Copolymerization	T (°C)	r_{AA}	r_{VAc}
Bulk[a]	70	10 ± 1	0.01 ± 0.01
In absolute ethanol[b]	75	3.2 ± 0.1	0.05 ± 0.01
Ethanol/water solution (93/7 w/w)[c]	75	2.6 ± 0.5	0.04 ± 0.01
Ethanol/water solution (1/1 w/w)[b]	75	0.96 ± 0.02	0.06 ± 0.01

[a]Bourdais [1].
[b]Nesterova et al. [3].
[c]Values obtained in this work with the Kelen–Tüdös method.

shown that the precision of experimentally determined reactivity ratios depends on such factors as the experimental design and the technique used to analyse the data [9,12,13]. Tidwell and Mortimer [12] pointed out the defects of different methods, including those of the Finema–Ross procedures. Non-linear least squares analysis has been shown to yield more precise reactivity ratio estimates than other commonly used methods, especially when experiments have not been well designed from a statistical point of view [13].

The results reported in the literature indicate that with the linearized form of the copolymer equation, the calculated values of r_2 and r_1 clearly depend on which monomer one selects as M_1. (In our case, acrylic acid was selected as monomer 1.) Furthermore, sometimes this procedure leads to negative values for the reactivity ratios, a result which is a physical impossibility.

The graphically valuable linear method (Kelen–Tüdös) allows rapid and reliable determination of the reactivity ratios and can also be applied for the estimation of the appropriateness of the composition equation, i.e. the assumed mechanism, of the copolymerization.

In this work the selected reactivity ratio values were those obtained with the Kelen–Tüdös method.

Table 3 shows that the copolymerization in ethanol decreases the reactivity ratios of acrylic acid, when compared to bulk. The presence of water increases this effect. The reactivity ratios for AA, obtained in the azeotropic ethanol/water solutions, are smaller than those in absolute ethanol, reported by Nesterova et al. [3]. Nevertheless, the former values are higher than those in ethanol/water (1/1 w/w) solutions.

The different reactivity ratio for AA in mixtures of ethanol/water is believed to be due to resonant and polar effects. It is known that the carbonyl group of AA, which is electron withdrawing, raises the polarizability of the carbon–carbon double bond. Solvents capable of forming hydrogen bonds with AA (for example water, ethanol), make the interaction with the carbonyl group stronger, and then cause a greater polarizability of the carbon–carbon double bond [4,14].

Conclusions

The copolymerization reactivity ratios for acrylic acid ($r_{AA} = 2.6 \pm 0.5$) and vinyl acetate ($r_{VAc} = 0.04 \pm 0.01$) in azeotropic ethanol/water (93/7 w/w) solutions at 75 °C were determined. The reactivity ratio values are within the range of those values reported in the literature in similar conditions.

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References

1. Bourdais, J., *Bull. Soc. Chim. Fr.*, 1955, 485.
2. Kerber, R., *Macromol. Chem.*, 1960, **96**, 30. Nikolaev, A.F. and V.M. Galpierin, *Visokomoliek. Soed.*, 1967, **A9**(11) 2469.
3. Nesterova, V.I., Meiya, N.V. and Pozdniakova, F.O., *Plastecheskie Massy*, 1974, **6**, 6.
4. Heublein, B. and Heublein, G., *Acta Polymerica*, 1988, **39**(6), 326.
5. Heublein, B. and Heubleuin, G., *Acta Polymerica*, 1988, **39**(6), 324.
6. *Encyclopedia of Polymer Science and Technology*, Vol. 1, 2nd edn, Wiley, New York, 1964, p. 217.
7. Reyes, B., Lima, E., Iglesias, G. and Hernández, C., Determination of reactivity rations in copolymerization, Thesis, Havana, 1989.
8. Kelen, T. and Tüdös, F., *Reaction Kinetics and Catalysis Letters*, 1974, **1**(4), 487.
9. Tidwell, P. and Mortimer, G., *J. Polym. Sci.*, 1965, **A3**(1), 369.
10. Fineman, M. and Ross, S.D., *J. Polym. Sci.*, 1950, **5**, 269.
11. Mayo, F.R. and Lewis, F.M., *J. Am. Chem. Soc.*, 1944, **66**, 1594.
12. Tidwell, P. and Mortimer, G., *J. Macromol. Sci. Rev. Macromol. Chem.*, 1970, **C4**(2), 281.
13. McFarlane, R.C., Reilly, P.M. and O'Driscoll, K.F., *J. Polym. Chem. Ed.*, 1980, **18**, 251.
14. Zaldivar, C., Iglesias, G., Suzarte, A. and Pinto, J.C., Polymer, (1996), submitted for publication.