Effect of pH on the Reactivity Ratios in the Copolymerization of Acrylic Acid and Acrylamide*

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Synopsis

The content of acrylic acid and acrylamide in their copolymers can be controlled by changing pH. The reactivity ratio of acrylic acid decreases with increasing pH, while the reactivity ratio of acrylamide increases with increasing pH. At low pH values, acrylamide is present in its protonated form which causes its reactivity to be low whereas at high pH values the reactivity of acrylic acid is decreased owing to its dissociation. When the monomer and radical approach each other, the acrylate anion becomes the least reactive species because of its symmetrical charge distribution, like charge repulsion and barium ion screening effect. HMO calculations were performed for models of all monomers and polymer radicals involved in copolymerizations. The experimental results concerning the reactivity of acrylic acid and acrylamide in copolymerization and the observed reactivity ratios were discussed on the basis of HMO calculations and resonance and Coulomb electrostatic effects. The observed reactivity ratios were correlated with the calculated differences in resonance energies computed for the models of transition states involved in copolymerizations.
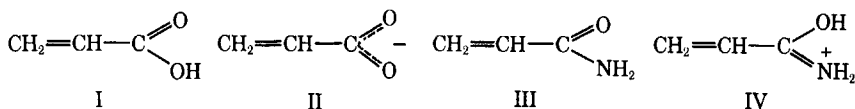
INTRODUCTION

In recent years, studies of the relative reactivity of radicals and monomers in copolymerizations have provided a great amount of information concerning the effects of the structure upon the course of free radical reactions. A key to the problem of copolymer composition is the recognition that the reactive properties of a growing polymer chain depend on the monomer unit at the growing end and in some cases the penultimate unit. The latter effect may become important in the copolymerization of monomers which contain highly polar or ionizable groups.[1] Under the conditions of high acidity or high basicity a given charge environment will exist about the growing polymer radical. Thus the charge on the last unit in the chain and the penultimate unit are important. In this work no attempt was made to evaluate penultimate effects.

In connection with our attempts to synthesize polyampholytes containing both acidic and basic functional groups along the polymer chain, the present paper reports the effect of changing of the pH value of the medium upon the relative reactivities of a growing polymer chain where the last unit is derived from an acrylic acid, acrylate anion, acrylamide, or protonated acrylamide free radicals, the structures of the monomers and polymer radicals involved in copolymerization reactions being as shown (I–VIII).

Monomer:

$$CH_2{=}CH{-}C{\overset{\displaystyle O}{\underset{\displaystyle OH}{\big\langle}}} \qquad CH_2{=}CH{-}C{\overset{\displaystyle O}{\underset{\displaystyle O}{\big\langle}}}{-} \qquad CH_2{=}CH{-}C{\overset{\displaystyle O}{\underset{\displaystyle NH_2}{\big\langle}}} \qquad CH_2{=}CH{-}C{\overset{\displaystyle OH}{\underset{\displaystyle {+}NH_2}{\big\langle}}}$$

I   II   III   IV

Polymer radical:

$$\overset{\displaystyle \cdot}{\sim\!\!\sim CH}{-}C{\overset{\displaystyle O}{\underset{\displaystyle OH}{\big\langle}}} \qquad \overset{\displaystyle \cdot}{\sim\!\!\sim CH}{-}C{\overset{\displaystyle O}{\underset{\displaystyle O}{\big\langle}}}{-} \qquad \overset{\displaystyle \cdot}{\sim\!\!\sim CH}{-}C{\overset{\displaystyle O}{\underset{\displaystyle NH_2}{\big\langle}}} \qquad \overset{\displaystyle \cdot}{\sim\!\!\sim CH}{-}C{\overset{\displaystyle OH}{\underset{\displaystyle {+}NH_2}{\big\langle}}}$$

V   VI   VII   VIII
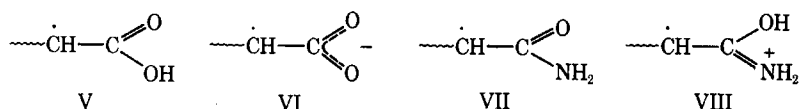
In this case, the dependence of the relative reactivities on pH is due to the dissociation of acrylic acid and protonation of acrylamide. At pH values lower than 2.0 acrylic acid exists in its undissociated form, whereas at pH values higher than 6.0 it exists in its ionized form as the acrylate anion. In both cases the system undergoes a simple copolymerization of acrylic acid and protonated acrylamide or acrylate anion and acrylamide, respectively. On the other hand, in the pH range between 2.0 and 6.0, the system undergoes terpolymerization.

It is well known that the simple Hückel molecular orbital (HMO) method has proven very useful in semiquantitative predictions of chemical reactivity of conjugated systems.[2–6] A few successful applications of the HMO method to several topics in free radical polymerization have also been reported.[7–10] In this paper the applicability of the HMO method for the calculation of monomer reactivity ratios has been explored. A theoretical analysis of the results has been undertaken in order to discuss the experimental reactivity ratios.

METHODS

HMO Treatment

Models of systems I–VIII were treated by the HMO (Hückel molecular orbital) method by using a CDC 3100 computer. π-Orbital energies, orbital expansion coefficients, bond orders, π-electron densities, and various derived quantities were obtained in the usual way by matrix diagonalization utilizing a standard program. The following values of the semiempirical parameters were adopted in the calculations:[3–10]

(a) Copolymerization of acrylic acid and protonated acrylamide:

Monomers   Radicals
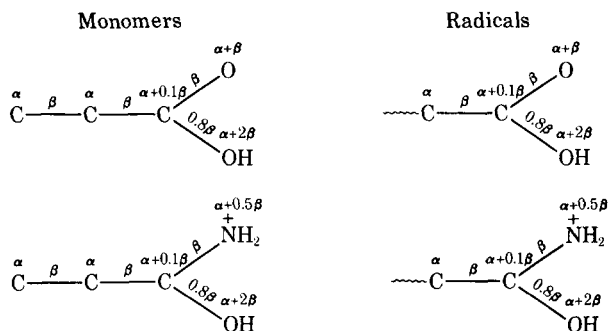
(b) Copolymerization of barium acrylate and acrylamide:

Monomers   Radicals
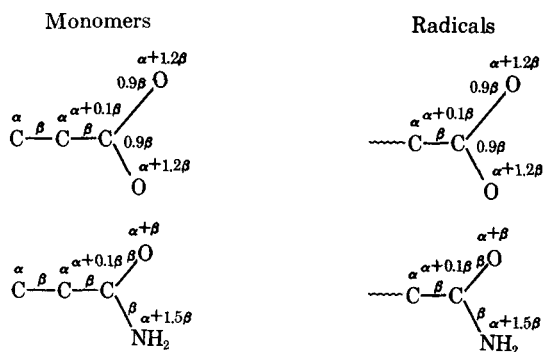
Here α is the Coulomb integral for the $2p_z$ atomic orbital of carbon, β is the resonance integral for the C-C bond in planar conjugated hydrocarbons, and the Coulomb integrals and resonance integrals of atoms in the models under study are given in the form $\alpha_X = \alpha + \delta_X\beta$ and $\beta_{CX} = \rho_{CX}\beta$, respectively, where δ_X and ρ_{CX} are numerical constants.

The energy characteristics of the systems I–VIII are summarized in Table I, and the π-electron densities and bond orders are shown in molecular diagrams in Figures 1 and 2.

EXPERIMENTAL

Materials

Commercial acrylic acid (Eastman Organic Chemicals) was purified by distillation under reduced pressure; bp 35°C/12 mm, n_D^{24} 1.4222. Commerical acrylamide (Eastman Organic Chemicals) was purified by recrystallization from benzene–ethyl acetate (7:3) three times and then dried in a vacuum oven; mp 84–85°C. Commercial barium hydroxide (J. T. Baker Chemical Co.) was recrystallized from water and had mp 78°C. The initiator was a 0.5 wt-% aqueous solution of potassium persulfate (J. T. Baker Chemical Co.), and the inhibitor was a 2.5 wt-% aqueous

TABLE I
Energy Characteristics for Systems I–VIII (β Units)[a]

No.	System	m	n	E_π	DE	k_1	k_{-1}
Monomers							
I	Acrylic acid	5	6	10.12192	0.82875	1.00000	−0.40146
II	Acrylate anion	5	6	8.95258	0.97004	1.04487	−0.41101
III	Acrylamide	5	6	9.37227	1.07910	1.00000	−0.47391
IV	Acrylamide (protonated)	5	6	9.38027	0.74066	0.79513	−0.49753
Polymer radicals							
V	Acrylic acid	4	5	8.38463	1.09146	0.41315	−1.29889
VI	Acrylate anion	4	5	7.20038	1.21784	0.41829	−1.30934
VII	Acrylamide	4	5	7.60662	1.31345	0.36661	−1.38661
VIII	Acrylamide (protonated)	4	5	7.68908	1.04948	0.23453	−1.36181

[a] m = number of π-electron centers; n = number of π-electrons in conjugation; E_π = the total π-electronic energy; DE = the delocalization energy; k_1 k_{-1} = the energies of the highest occupied and of the lowest vacant π-molecular orbital, respectively. Additional HMO data are available at request from the authors (C. P.).
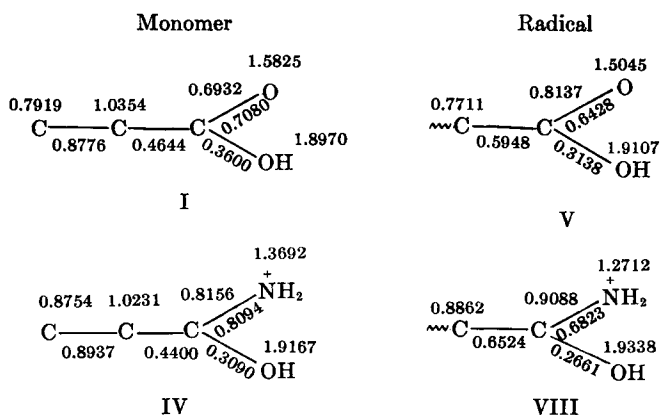
Monomer

Radical

1.5825

0.7919   1.0354   0.6932   O
                            0.7080
C———C———C 0.7080
    0.8776   0.4644   0.3600   1.8970
                            OH

I

1.5045

0.7711   0.8137   O
                    0.6428
~~C———C 0.6428
    0.5948   0.3136   1.9107
                    OH

V

1.3692
        +
0.8754 1.0231 0.8156 NH₂
                    0.8094
C———C———C 0.8094
    0.8937   0.4400   0.3090   1.9167
                            OH

IV

1.2712
        +
0.8862   0.9088   NH₂
                    0.6823
~~C———C 0.6823
    0.6524   0.2661   1.9338
                    OH

VIII

Fig. 1. Molecular diagrams of the structures involved in the copolymerization of acrylic
acid and acrylamide. π-Electron densities and bond orders are shown.

Monomer

1.7375

0.7935   1.0356   0.6959   O
                            0.5651
C———C———C 0.5651
    0.8808   0.4586   0.5651   1.7375
                            O

II

Radical

1.7187

0.7560   0.8066   O
                    0.5127
~~C———C 0.5127
    0.5747   0.5127   1.7187
                    O

VI

1.6444

0.8196   1.0360   0.7145   O
                            0.6470
C———C———C 0.6470
    0.8944   0.4332   0.5118   1.7855
                            NH₂

III

1.5938

0.7918   0.8131   O
                    0.5964
~~C———C 0.5964
    0.5615   0.4569   1.8013
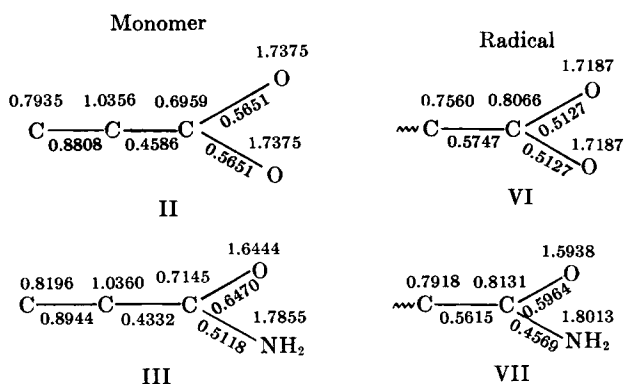   NH₂

VII

Fig. 2. Molecular diagrams of the structures involved in the copolymerization of barium
acrylate and acrylamide.

solution of hydroquinone (Eastman Organic Chemicals).   A 10-ml portion
of both the initiator and inhibitor solutions was used in each experiment.

Samples

The approximate pH values of the samples were obtained by adding
barium hydroxide to defined mixtures of the monomers in water.   The
mixtures were then centrifuged and filtered, and the pH was adjusted to
the desired value by adding the necessary amount of saturated aqueous
solution of barium hydroxide.   The concentration of acrylic acid in these
mixtures varied from $0.01102M$ to $0.002813M$ and the corresponding acryl-
amide concentrations were so chosen that the feed ratio values (acrylic
acid:acrylamide) varied between 4:1 and 1:4.   A Beckman expanded-
scale pH-meter was used to determine the exact pH values.   The total
volume of each sample was 90 ml.   The samples were poured into screw-cap
bottles and nitrogen was bubbled through the solutions for about 10 min.

Copolymerization Procedure

The screw-cap bottles with samples were placed in a water bath and copolymerizations were carried out at 60 ± 0.1°C with potassium persulfate as the initiator and hydroquinone (added at the end of the polymerization) as the inhibitor of the reaction.[11] Then the barium ions in the polymer solutions were precipitated by adding $1N$ sulfuric acid, the precipitates were centrifuged and separated, and the solutions were concentrated under reduced pressure to 15–20 ml. The concentrated solutions were poured into 200 ml of methanol, the precipitated copolymers were dissolved in water, reprecipitated twice with methanol, and dried for 24 hr in a vacuum oven.

The results showing the yields of the copolymer at different pH values and feed ratios are shown in Table II.

TABLE II
Conversion in Copolymerization of Acrylic Acid and Acrylamide at 60°C

pH	Conversion at various feed ratios,[a] %				
	4:1	2:1	1:1	1:1.85	1:4
2.17	3.92	2.54	4.30	10.7	4.46
3.77	1.49	0.81	1.36	3.52	7.01
4.25	3.26	3.36	0.94	0.45	4.27
4.73	0.30	1.62	2.73	4.14	2.67
6.25	0.35	0.57	2.50	1.19	3.41

[a] Acrylic acid: acrylamide.

Analysis

The composition of the copolymers was determined from their nitrogen content using the semi-micro Kjeldahl method with selenium as the digestion catalyst.[11] The percentage of nitrogen and the molar content of acrylamide in copolymers are summarized in Table III.

RESULTS AND DISCUSSION

The course of many radical reactions including copolymerizations is fairly independent of the medium in which these reactions take place (cf., eg., copolymerization of styrene and methyl methacrylate[12]). The copolymerization of acrylic acid and acrylamide is an exception in this respect,[13,14] the change in reactivity ratios being due to the dissociation of acrylic acid and protonation of acrylamide at certain pH values.

Our experimental results obtained in the copolymerization of acrylic acid and acrylamide are summarized in Table III showing the percentage of nitrogen and the mole percent of acrylamide at different pH values and feed ratios. The effect of pH upon the reactivity ratios r_1 and r_2 thus obtained (the subscripts 1 and 2 refer to acrylic acid and acrylamide, respectively) is shown in Table IV.

TABLE III

Composition of the Copolymer Obtained from Acrylic Acid and Acrylamide at 60°C and Various Feed Ratios[a]

pH	4:1		2:1		1:1		1:1.85		1:4	
	N, %	Acrylamide, mole-%	N, %	Acrylamide, mole-%	N, %	Acrylamide, mole-%	N, %	Acrylamide, mole-%	N, %	Acrylamide, mole-%
2.17	2.47	12.51	4.56	23.12	7.00	35.49	9.86	50.03	13.12	66.54
3.77	5.16	26.17	7.49	38.01	9.84	49.93	12.09	61.34	14.33	72.70
4.25	6.06	30.77	8.28	42.01	10.64	53.99	12.88	65.35	15.22	77.22
4.73	6.11	31.00	8.94	45.36	11.44	58.04	13.66	69.28	15.56	81.16
6.25	7.10	36.02	9.84	49.94	12.46	63.21	14.77	74.93	16.81	85.31

[a] Acrylic acid : acrylamide.

The monomer reactivity ratios were calculated from the copolymer composition eq. (1) according to Alfrey and Goldfinger,[15]

$$f_1(1 - 2F_1)/(1 - f_1)F_1 = r_1 + f_1^2(F_1 - 1)/(1 - f_1^2)F_1r_1 \qquad (1)$$

where f_1 and F_1 are the corresponding mole fractions in the monomer and copolymer, respectively. The Lewis-Mayo plots of r_1 against r_2 for different feed ratios and given pH values are shown in Figures 3–7. In Figure 8, the effect of pH change is shown for both r_1 and r_2. The crossover point of equal reactivity occurred at pH 3.77 ($r_1 = r_2 = 0.56$).

TABLE IV
Reactivity Ratios for Acrylic Acid (r_1)
and Acrylamide (r_2) at Different pH Values

pH	r_1	r_2
2.17	1.73 ± 0.21	0.48 ± 0.06
3.77	0.56 ± 0.09	0.56 ± 0.09
4.25	0.45 ± 0.03	0.67 ± 0.04
4.73	0.42 ± 0.02	0.95 ± 0.03
6.25	0.35 ± 0.03	1.32 ± 0.12

For the copolymerization carried out at 60°C and pH 2.17, our values of reactivity ratios for acrylic acid and acrylamide were $r_1 = 1.73$ and $r_2 = 0.48$, respectively. Bourdais[14] reported $r_1 = 1.43$ and $r_2 = 0.60$ at 25°C for an aqueous system initiated by potassium metabisulfite and persulfate, whereas the values obtained by Smets and Hesbain[13] for the copolymeriza-
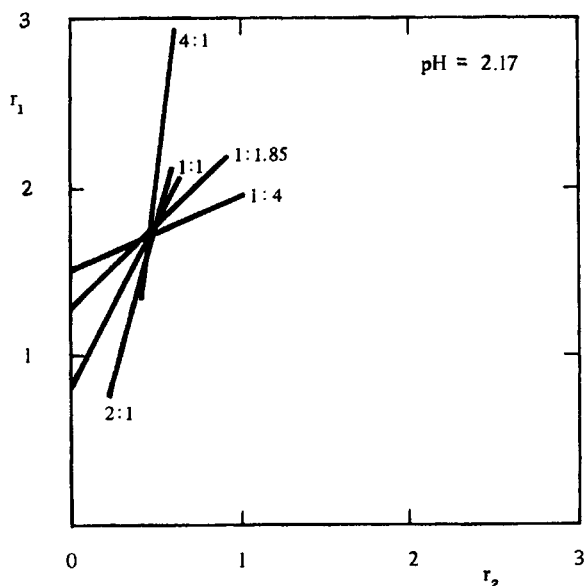

Fig. 3. Plot of reactivity ratios r_1 against r_2 at pH 2.17 and different feed ratios.
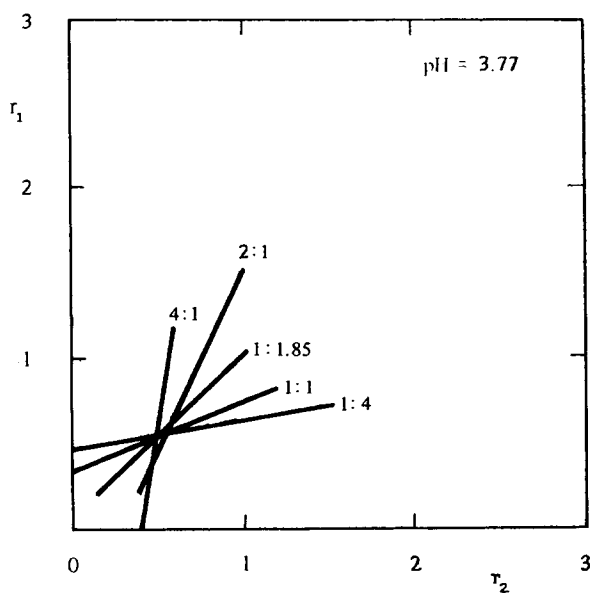
Fig. 4. Plot of reactivity ratios r_1 against r_2 at pH 3.77 and different feed ratios.
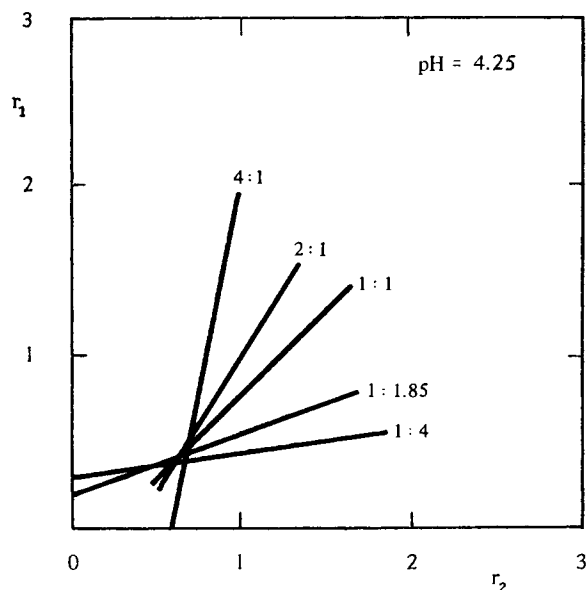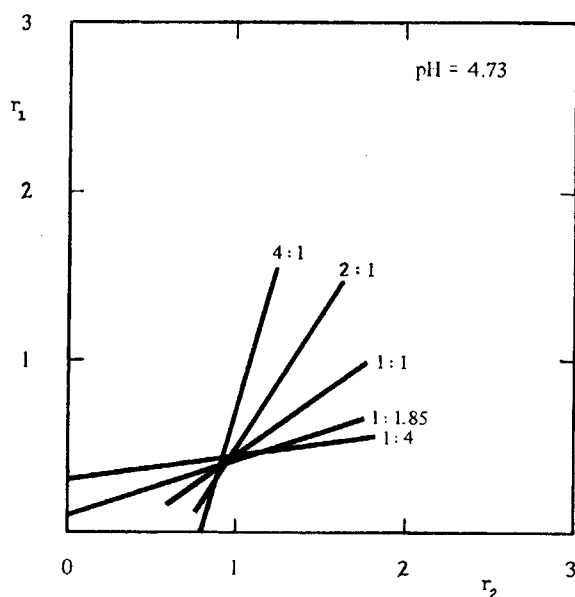

Fig. 5. Plot of reactivity ratios r_1 against r_2 at pH 4.25 and different feed ratios.

tion in benzene solutions at 60°C initiated by azobisisobutyronitrile were $r_1 = 0.36$ or $r_2 = 1.38$, respectively. Thus, our values for an aqueous system and the reported values for a benzene solution are almost reversed.

The reactivity of a monomer in copolymerization is determined by the nature of the substituents on the double bond.[16] A comparison of the pos-

Fig. 6. Plot of reactivity ratios r_1 against r_2 at pH 4.73 and different feed ratios.
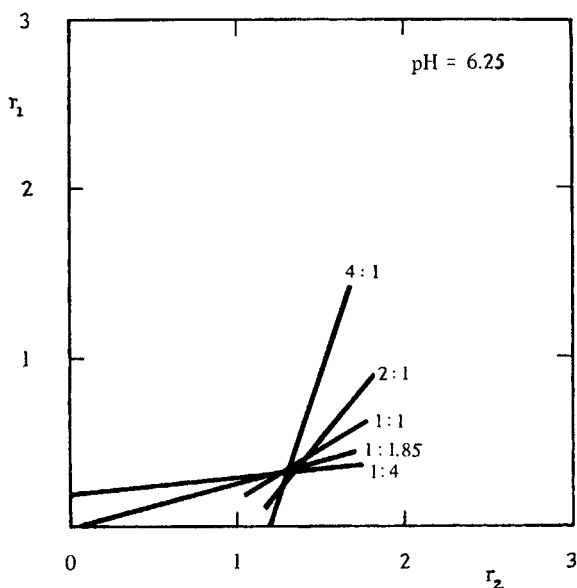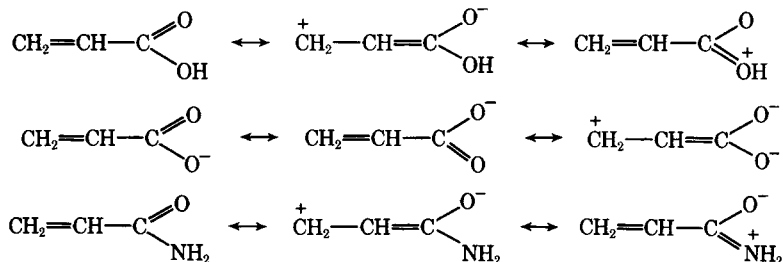

Fig. 7. Plot of reactivity ratios r_1 against r_2 at pH 6.25 and different feed ratios.

sible resonance forms of acrylic acid, acrylate anion, and acrylamide studied in the present work shows that all these systems possess three main resonance structures and that the acrylate anion is more resonance stabilized than acrylic acid because of a more symmetric charge distribution. On the other hand, when comparing the three possible resonance forms of acrylic
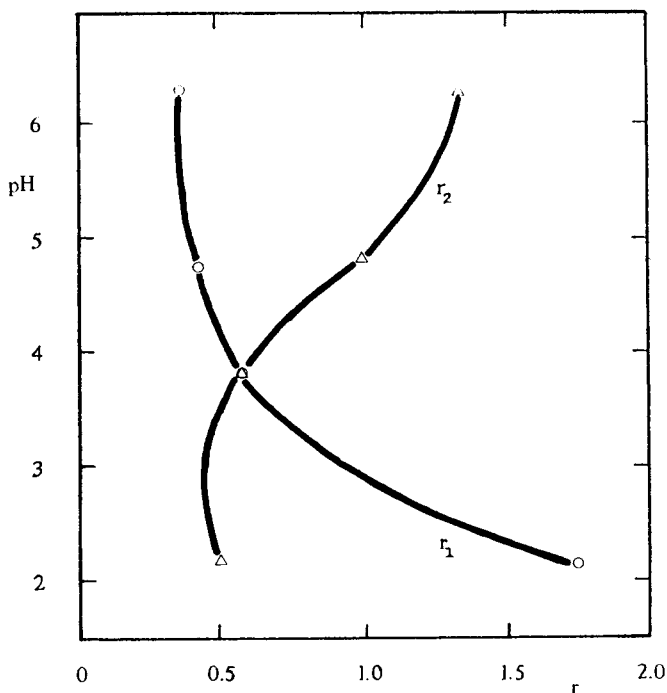
Fig. 8. Reactivity ratios r_1 and r_2 plotted vs. pH.

acid and acrylamide, it becomes obvious that acrylamide is more resonance-stabilized than acrylic acid, whose one resonance form bears a positive charge on electronegative oxygen. Thus, the effects of the substituents on the double bond in monomers in the order of decreasing reactivity are $CONH_2 \sim COO^- > COOH$.

$$CH_2=CH-C\overset{O}{\underset{OH}{\big\langle}} \quad \leftrightarrow \quad \overset{+}{CH_2}-CH=C\overset{O^-}{\underset{OH}{\big\langle}} \quad \leftrightarrow \quad CH_2=CH-C\overset{O}{\underset{+OH}{\big\langle}}$$

$$CH_2=CH-C\overset{O}{\underset{O^-}{\big\langle}} \quad \leftrightarrow \quad CH_2=CH-C\overset{O^-}{\underset{O}{\big\langle}} \quad \leftrightarrow \quad \overset{+}{CH_2}-CH=C\overset{O^-}{\underset{O^-}{\big\langle}}$$

$$CH_2=CH-C\overset{O}{\underset{NH_2}{\big\langle}} \quad \leftrightarrow \quad \overset{+}{CH_2}-CH=C\overset{O^-}{\underset{NH_2}{\big\langle}} \quad \leftrightarrow \quad CH_2=CH-C\overset{O^-}{\underset{+NH_2}{\big\langle}}$$

Similarly, the reactivity of a polymer radical is determined by the substituent on the radical. Substituents which increase the reactivity of double bonds greatly decrease the reactivity of resulting radicals. This effect of substituents upon decreasing the reactivity of a radical is much greater than its effect upon enhancing the reactivity of the monomer.[16] Thus, resonance stabilization decreases the reactivity of radicals so that their order of reactivity is $COOH > COO^- \sim CONH_2$.

According to Evans[7] (cf. also Flory[17]), resonance stabilization of monomers and radicals can be considered in terms of a potential energy diagram (cf. Fig. 3 in ref. 7), where the potential energy is plotted against the distance of separation of reactants. The energy change for the addition of a monomer to a radical can be expressed as the heat of reaction, $-\Delta H_p$, given as

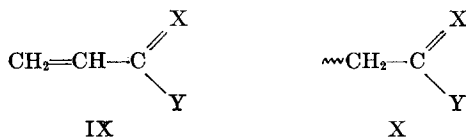$$-\Delta H_p = -(\Delta H_p{}^\circ) + U_p - U_m - U_a \qquad (2)$$

where U_p, U_m, and U_a are the resonance energies for the product radical, the monomer, and the attacking radical, respectively; $\Delta H_p{}^\circ$ is the σ-component of the heat of reaction. It should be pointed out that, in spite of the fact that the reaction rate of copolymerization does not depend on the heat of the reaction but on the energy of the transition state, the activation energies can be correlated with the heats of reactions in a series of similar reactions.[7,17]

Using eq. (2), we have estimated the heats of reactions under study. For this purpose, the resonance energies U_a, U_m, and U_p of radicals and monomers were calculated by the HMO method and are expressed as delocalization energies DE in Table I, where DE is the additional bonding energy resulting from delocalization of electrons originally constrained to isolated double bonds.

Thus,

$$DE = E_\pi - E_R \qquad (3)$$

where E_R is the energy of the corresponding reference state with localized electrons. The models of localized structures used in this calculation were of the types IX and X for monomers and polymer radicals, respectively,

$$\text{CH}_2\text{=CH—C}\overset{\displaystyle X}{\underset{\displaystyle Y}{\Big\langle}} \qquad \text{⟋⟋CH}_2\text{—C}\overset{\displaystyle X}{\underset{\displaystyle Y}{\Big\langle}}$$

IX   X

where X = O or $\overset{+}{\text{N}}\text{H}_2$ and Y = OH or NH_2, and the values of Coulomb integrals used in the computation remained unchanged (for examples of calculations of delocalization energies of conjugated systems containing heteroatoms, see Riggs[18]). The $\Delta H_p{}^\circ$ term in eq. (2) was neglected in the calculations.

The calculated values of ΔH_p (in β units) are given in Table V. It follows from the previous discussion that the higher the heat of the reaction, the lower the activation energy E_a.

At higher pH values, a copolymerization of acrylamide and barium acrylate can be considered. Thus, a comparison of the values in the second and third row of Table V reveals that acrylamide radical needs less activation energy to react with its own monomer than with barium acrylate, while barium acrylate radical needs a greater activaion energy to react

TABLE V
Heats of Reaction ΔH_p (β units)[a]

Polymer radical	ΔH_p			
	Acrylic acid	Acrylate anion	Acrylamide	Acrylamide (protonated)
Acrylic acid	0.8275	—	—	0.78264
Acrylate anion	—	0.97004	0.98349	—
Acrylamide	—	1.06565	1.07910	—
Acrylamide (protonated)	0.78677	—	—	0.74066

[a] Calculated by eq. (2).

with its own monomer than with acrylamide. On the other hand, a comparison of the respective columns shows that acrylamide monomer is more reactive when the last unit of the growing chain is acrylamide. In the case of barium acrylate, it is easier for the reaction to occur with acrylamide radical. Thus, the total probability of acrylamide appearing in the copolymer obtained at higher pH values is greater than unity whereas the reactivity ratio of barium acrylate should be less than one.

Similarly, the first and the fourth row of Table V can be used for the copolymerization of acrylic acid and protonated acrylamide at low pH values. Acrylic acid radical is more reactive toward acrylic acid than toward acrylamide monomer whereas acrylamide radical is less reactive toward acrylamide monomer than it is toward acrylic acid. Thus the reactivity ratio of acrylic acid should be greater than unity and that of acrylamide should be smaller than one.

Reactivity ratios are ratios of two rate constants, and thus they can be calculated from the difference in activation energies.[8-10] Assuming a linear relationship between the activation energies E_a and the respective heats of copolymerization $-\Delta H_p$, there also should be a linear correlation between log r and the difference in calculated heats of copolymerization, $\Delta(\Delta H_p)$, obtained from the values of $-\Delta H_p$ computed by using eq. (2) and given in Table V. Thus,

$$\log r_{exp} = a\Delta(\Delta H_p)(\beta) + b \qquad (4)$$

where a is the proportionality constant and b is the intercept with the y axis. By definition, for all pairs in which the radical and monomer are of the same species, the reactivity ratios are one and thus log $r = 0$ and $\Delta(\Delta H_p) = 0$. A plot of log r_{exp} versus $\Delta(\Delta H_p)$ is shown in Figure 9.

In spite of the relatively small number of experimental data, a possibility of a correlation between the reactivity ratios r_{exp} and the calculated $\Delta(\Delta H_p)$ values has been explored. By using the experimental values of reactivity ratios r_{exp} given in Table VI and the theoretical $\Delta(\Delta H_p)$ values calculated as differences in resonance energies from the data in Table V (cf. Table VI), the value of the constant a in eq. (4) computed by the least-squares method is 7.25, and the value of the constant b is -0.08 (in an ideal case, $b = 0$).
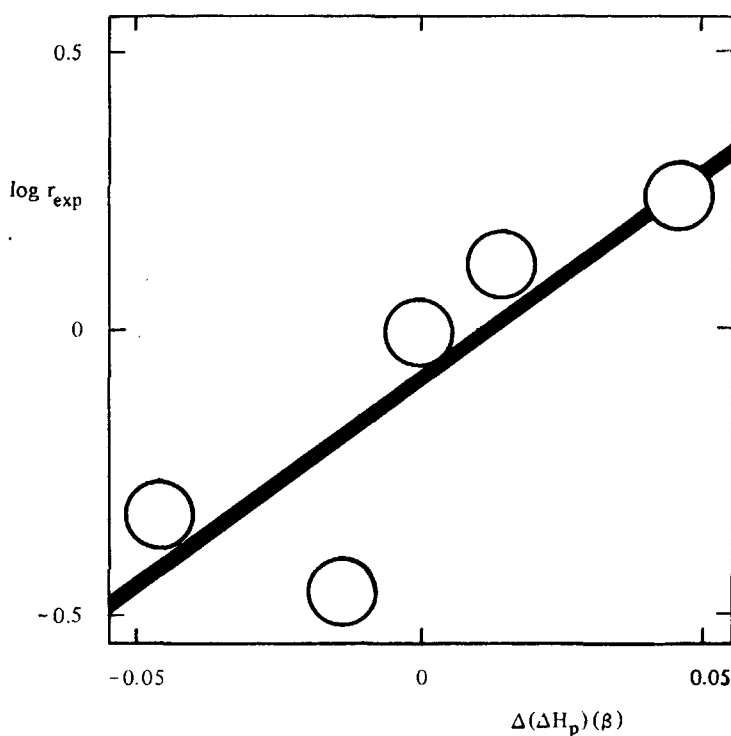
Fig. 9.   Observed reactivity ratios (log r_{exp}) plotted against calculated differences in conjugation energies, $\Delta(\Delta H_v)(\beta)$.

$$\log r = 7.25\ \Delta(\Delta H_p)(\beta) - 0.08 \qquad (5)$$

where number of points $n = 5$.

It seems worthwhile to summarize the values of r_{calc} obtained by substituting the appropriate $\Delta(\Delta H_p)$ values into eq. (5) in Table VI.

Coulomb electrostatic forces are one of the important factors influencing the reactivity of acrylic acid and acrylamide at different pH values. At low pH values, the zwitterion form of acrylamide may become protonated[19,20] to give a monomer IV or a polymer radical VIII with a formal positive charge. Since both the monomer IV and the radical VIII bear

TABLE VI
Experimental and Calculated Reactivity Ratios

Compound	r_{exp}	$\Delta(\Delta H_p)^a$	r_{calc}^b
Acrylic acid	1.73 ± 0.21	0.04611	1.78
Barium acrylate	0.35 ± 0.03	−0.01345	0.38
Acrylamide	1.32 ± 0.12	0.01345	1.03
Acrylamide (protonated)	0.48 ± 0.06	−0.04611	0.66

[a] Cf. Table V.
[b] From eq. (5).

like charges, they repel each other, whereas both the monomer and the radical of acrylic acid exist in their uncharged, undissociated forms which may react freely. In agreement with this, the reactivity ratio of acrylic acid should be greater than that of acrylamide at low pH values. On the other hand, at high pH values acrylamide exists as a neutral, uncharged species whereas acrylic acid is present in the form of barium acrylate. The situation is thus reversed and the reactivity of barium acrylate is decreased when compared with the reactivity of acrylamide.

The reactivity ratios change reversibly by transforming acrylic acid into barium acrylate and vice versa (acrylic acid is 25, 50, 75, and 99% ionized at pH 3.77, 4.25, 4.73, and 6.25, respectively). The effect of barium ion is that of an increased repulsion between the acrylate anion of the monomer and the radical (for a similar effect of alkali metal ions, cf. Wojnarowski[21]). The content of acrylamide in the copolymer increases with increasing pH similarly as in other related copolymerizations.[14,21,22]

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