Copolymerization of Methacrylic Acid and N-Vinylpyrrolidone in Aqueous Solution

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ABSTRACT

The monomer reactivity ratios for the copolymerization of
methacrylic acid (MA) and N-vinylpyrrolidone (NVP) in
aqueous media at 30°C were determined as a function of pH
(range 2-10), by use of both the modified differential (YBR)
and integrated copolymerization equation to process the data
at high conversions ($< 70\%$ by weight). The reactivity ratio
r_1 (for MA) ranges from 0.92 to 8.3 and that for NVP (r_2)
is very small except at pH 7 and 8. The r_1 values show
two minima: 2.9 at pH 4 and 0.92 at pH 8, nearly correspond-
ing to the pKa values of the monomer MA and the polymer,
respectively. Addition of 1 $\underline{M}$ sodium chloride results in an
increase of r_1 values, and the values are still lower than
those of the undissociated acid. The trend of r_1 with pH is
seen to follow that of the homopolymerization behavior of
MA reported in the literature. The r_1 and r_2 are of the same
order as those obtained in dimethylformamide in the literature.

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INTRODUCTION

Polymerization reactions of ionizing monomers in aqueous solution reveal additional interesting features [1, 2] in comparison with those of nonionic monomers. These features arise from the fact that the ionization of monomers causes electrostatic interaction between the monomer and the growing polymer chain. The growing polymer also could ionize, enhancing the electrostatic repulsion between the growing polymer and the monomer, thus considerably reducing the rate of addition of the latter. In the aqueous polymerization of methacrylic acid (MA) it was found [3] that the rate of polymerization decreased with increase in pH from 4 to 7, reaching a minimum at pH 6-7, then increased slowly as the pH is raised to 9, leveling off in the pH range 9-12. These interactions between the reacting species were considerably reduced [2] by the addition of an excess of a strong electrolyte, which provides an adequate screening of the charges on the monomer and the polymer. The polymerization rate then nearly attains its value in the absence of charge interactions. The present investigation was undertaken by us to study the copolymerization behavior of MA in aqueous solution, with a nonionic monomer like N-vinylpyrrolidone (NVP) at a series of pH values ranging from 2 to 10, to corroborate the earlier findings on the polymerization behavior of methacrylic acid. The monomer reactivity ratios obtained as a function of the pH of the medium would elucidate the reactivity of methacrylic acid at different degrees of ionization.

EXPERIMENTAL

Chemicals and Reagents

Methacrylic acid (commercial grade) containing 0.5% inhibitor was distilled under reduced nitrogen pressure and the middle cut, boiling at 60°C/12 Torr, was collected and stored in the cold at 0°C (mp 15°C). N-Vinylpyrrolidone (gift of BASF, Germany) was distilled under reduced nitrogen pressure and the fraction boiling at 96°C/14 Torr was collected and stored at 0°C (mp 13.5°C). The purity of both the monomers by the bromine addition method was found to be nearly 99.5% and above.

Potassium persulfate, sodium sulfite, and sodium chloride were A. R. grade. Acetone was purified and distilled by a standard procedure. Water used was doubly distilled over alkaline permanganate and was ion free.

Polymerization Procedure

The copolymerization reactions were conducted at 30 ± 1°C under a nitrogen atmosphere, with $K_2S_2O_8$-Na_2SO_3 as the initiator in aqueous solution at pH ranging from 2 to 10. The redox system operates in acid solutions, and in an alkaline medium (up to pH 13) the persulfate decomposes to give radicals [4-6]. The purified monomers, MA and NVP were taken in mole ratios 9:1, 7:3, 1:1, 3:7, and 1:9 in Corning glass reaction vessels. The pH adjustment was made by addition of conductivity water, followed by calculated amounts of standard sodium hydroxide solution. The final volume of the reaction mixture was made up to ca. 20 ml, such that the total monomer concentration was nearly 1 $\underline{M}$. Polymerizations were initiated after thermostatting each recipe, flushing with nitrogen for 15 min, and adding initiator at a concentration of 5×10^{-4} $\underline{M}$ at low pH and 2.5×10^{-3} $\underline{M}$ at high pH. The polymerization time ranged from 3 to 5 hr, and nitrogen flushing was stopped during the polymerization since traces of oxygen can slow down the rate [3].

Isolation of Polymers

Polymerization was stopped by the addition of a solution of hydroquinone such that its concentration was more than twice that of the initiator taken. Drops of 30% hydrochloric acid were added to bring the pH to 0. Each solution was evacuated at low pressure (ca. 10^{-2} Torr), keeping the temperature at 30°C. If necessary, some acetone was added to facilitate the removal of water. After the volume of each solution was reduced to < 5 ml, the polymer was precipitated by the addition of acetone (ca. 250 ml). The hydroquinone was removed by acetone, and the sodium ions originally introduced into the mixture were precipitated in the form of sodium chloride in the presence of acetone. The precipitated polymer was redissolved in a minimum amount of water and precipitated with acetone. This was carried out twice. The solids were quantitatively collected and dried under vacuum at 60°C to constant weight. The polymer obtained was in the acid form, and the amount of sodium chloride formed was calculated from the amount of NaOH introduced initially during the pH adjustment; the polymer weights were corrected accordingly. Blank runs with the monomer mixtures showed no polymerization during the isolation procedure described above. The sodium chloride which was formed along with the polymer was found to be quantitatively equivalent to the sodium hydroxide added during the pH adjustment and insoluble in the acetone rich-mixtures such as those used in these experiments (acetone:water 95:5).

The copolymer compositions were determined by nitrogen analysis by a semimicro Kjeldahl procedure [7]. The procedure gave a 15.1% error in the analysis of pure polyvinylpyrrolidone. This correction was made for all the copolymers. Such errors for polyvinylpyrrolidone were encountered earlier [8, 9].

Treatment of Data

The experimental data were treated by both the differential and integrated equations. The differential equation used was the modified Fineman and Ross equation suggested by Yezerielev et al. [10] with a least-squares procedure [10, 11] to fit the data. Since the polymerization conversions are as high as 70%, the experimental data of monomer feed, copolymer compositions, and the weight percent conversion, were treated by the Mayo and Lewis integrated copolymer equation [12] by using the computer procedure employed by Joshi [11] to solve for r_1 and r_2 values. A Honeywell model computer was used for calculations.

Table 1 presents the monomer reactivity ratios for the copolymerization of methacrylic acid and N-vinylpyrrolidone at different pH values ranging from 2 to 10 in water at 30°C. The r_1 refer to methacrylic acid and r_2 to N-vinylpyrrolidone.

DISCUSSION

The solutions for r_1 and r_2 obtained by the differential (YBR) and integral methods are not drastically different, in spite of conversions being as high as 60-70% in some experiments. In a good number of cases, the agreement is within 10% (Table 1). The close agreement between the differential YBR and the integrated equation procedure was pointed out by Joshi [11] after a survey of a large number of experimental data. However, for the present discussion, the data obtained by the solution of the integrated equation is considered primarily since the conversions are high.

The data clearly show a much faster rate of polymerization for MA at all pH levels than for NVP. At pH 7 and 8, NVP shows an enhanced rate. The r_1 drops from 6-8 at pH 2-3 to 2.9 at pH 4, at which 30% of the monomer is ionized (pKa of MA = 4.32) and continues to be low (r_1 = 4.9-4.0 in the pH range 5-7) (Table 1). However, at pH close to the value of pKa of poly(methacrylic acid) (7.0) [1], the r_1 drops to a minimum of 0.92 (at pH 8) when > 90% of the polyacid is ionized. The r_1 thereafter rises slowly to 3.6 when the pH is raised to 10. The r_1 is unaffected in the pH range 3-10 in the presence of 1 M NaCl, the value remaining fairly constant ($r_1 \simeq$ 4.9-4.4). This

TABLE 1. Monomer Reactivity Ratios for Copolymerization of Methacrylic Acid (M_1) and N-Vinyl-pyrrolidone (M_2) in Water at 30°C

pH	Differential method[a]		Integrated equation[b]		Conversion (wt %)	$R_p \times 10^5$ (mole/liter-sec)[c]
	r_1	r_2	r_1	r_2		
2	6.87(±0.39)	-0.035(±0.025)	6.49(±0.42)	-0.038(±0.028)	4.9-46	
3	8.62(±0.17)	-0.059(±0.005)	8.34(±0.14)	-0.006(±0.003)	6 -37	3.4
4	2.99(±0.18)	-0.035(±0.016)	2.99(±0.18)	-0.032(±0.015)	8.5-12	1.7
5	5.79(±1.11)	0.073(±0.106)	4.90(±0.91)	0.052(±0.086)	17 -70	0.57
6	4.33(±0.17)	-0.026(±0.009)	4.00(±0.102)	-0.027(±0.006)	4.8-61	0.11
7	4.17(±0.28)	0.291(±0.05)	4.03(±0.29)	0.28 (±0.062)	5.7-43	0.11
8	1.23(±0.52)	-0.011(±0.047)	0.92(±0.29)	0.67 (±0.19)	5.7-28	0.23
9	2.33(±0.39)	0.039(±0.065)	2.33(±0.38)	0.037(±0.062)	11.6-20	0.52
10	3.59(±0.23)	-0.313(±0.036)	3.58(±0.23)	-0.031(±0.035)	6 -22	0.98
3(1 M NaCl)	5.01(±0.42)	0.28 (±0.12)	4.90(±0.40)	0.27 (±0.12)	6.5-32	
7(1 M NaCl)	4.42(±0.38)	-0.084(±0.042)	4.44(±0.39)	-0.059(±0.044)	9 -31	
10(1 M NaCl)	4.45(±0.20)	-0.031(±0.02)	4.43(±0.19)	-0.030(±0.019)	4.3-23	
8	0.65	0.33[d]				
8(1 M NaCl)	0.92	0.33[d]				
Dimethyl-formamide	4.7	0.07[e]				

aCalculated according to refs. [10, 11].
bCalculated according to refs. [11, 12].
cThe rate of polymerization values deduced from Fig. 1 of ref. [1].
dObtained from Kabanov and Topchiev [2]; method of calculation not mentioned.
eObtained by Fineman-Ross method [13].

trend observed for the reactivity ratio correlates well with the homo-
polymerization behavior of methacrylic acid [1-3]. The homopolymer-
ization rate of methacrylic acid, as known, decreases with increasing
pH in the range 1-6, reaching a minimum at pH 6-7 and then increas-
ing slowly as the pH is raised from 7 to 12. The accepted explanation
[1-3] that the approaching monomer suffers electrostatic repulsion as
it ionizes (MA is 50% ionized at its pKa = 4.32) and the electrostatic
repulsion during the monomer addition is maximum when the meth-
acrylic acid unit in the polymer begins to ionize (the polymer is 50%
ionized at its pKa = 7.0) confirms with the observed trend in the r_1
values: namely, the r_1 reaches a minimum at a pH in the vicinity of
the pKa of the monomer and a minimum in the vicinity of pKa of the
polymeric acid. At pH 8.5, the electrostatic repulsion between the
monomer units in the polymer is maximum [1] and is also the repul-
sive interactions between the growing polymer chain and the approach-
ing monomer radical. At alkaline pH, the negative charges on the
carboxyls are partially shielded by the introduction of Na^+, resulting
in faster addition of the monomer and an increase in r_1. As seen in
Table 1, r_1 increases from 0.92 to 3.5 as the pH increases from 7 to
10. Values of r_1 = 0.65, r_2 = 0.33 and r_1 = 0.9, r_2= 0.33 were reported
[2] for the same system at pH 8 in the absence and presence of 1 $\underline{M}$
NaCl, respectively. The method of computation of r_1 and r_2 was $\overline{not}$
mentioned, and the increase of r_1 was not much in the presence of
NaCl [2]. A significant increase in r_1 is noted in the presence of NaCl
at alkaline pH; the values are comparable to those at pH 5-7. The r_1
values in presence of NaCl, however, do not equal those at low pH,
presumably because the added NaCl disrupts the hydrophobic bonds
and the hydrogen bond formation between the methacrylic acid mole-
cules responsible for high rate of polymerization in acid medium. It
is known that methacrylic acid exists as a dimer through hydrogen
bond and hydrophobic bond formation in acid medium [13].

It is assumed, however that the pKa of the copolymer of MA and
NVP is in the vicinity of that of pure poly(methacrylic acid), since
most of the copolymers obtained are richer in the acid. The reactiv-
ity ratios of NVP are slightly positive or slightly negative and together
with the standard deviations they may be taken to the zero. The rela-
tively high values of 0.28 and 0.67 at pH 7 and 8 respectively for r_2
may be due to the fact that the rate of addition of methacrylate ions
to the polymeric macroradicals, which are also fully ionized, is
minimum in this range (see R_p values of Table 1), and hence a vinyl-
pyrrolidone molecule will have a greater chance of addition, yielding
copolymers richer in NVP. However, this situation will change at
higher pH, when the Na^+ counterions begin to shield the charge on the
carboxylate ions.

The values of r_1, r_2 obtained in the present study seem to be in
agreement with the recent values obtained by Chapiro [14] for the
copolymerization of MA and NVP in dimethylformamide, which is

a basic solvent, although the comparison should be treated with caution since the Fineman and Ross treatment applied [14] therein to obtain the results is inadequate in comparison with the YBR differential and Mayo-Lewis integrated equation. Similar caution should be exercised in comparing the results of the present study with those of Kabanov et al. [2], who have not stated the computation procedure adopted by them.

CONCLUSION

The copolymerization behavior of methacrylic acid with a nonionic monomer like N-vinylpyrrolidone in aqueous solution shows a strong dependence on the pH of the reaction medium, following the same trend known for the homopolymerization of the acid. The reactivity of MA is lowest at the pH corresponding to the near complete ionization of poly(methacrylic acid). The reactivity of MA also decreases as the monomer ionizes. These trends, as in the case of homopolymerization, are understood in terms of the electrostatic interactions between the ionizing monomer and the growing polymer, which also subsequently ionizes at higher pH. Addition of a strong electrolyte largely suppresses these interactions, raising the reactivity ratio to a value much higher than the minimum.

ACKNOWLEDGMENT

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