

Copolymerization of *Cis*-Butenedioic Acid with Sodium Methallylsulfonate in an Aqueous Solution

YAO KEJUN, QIN ZENQUAN, and YE CHUANYAO, *Institute of Colloidal and Interfacial Chemistry, Shandong University, Jinan, Shandong, People's Republic of China*

Synopsis

Water-soluble copolymers of *cis*-butenedioic acid (MA) with sodium methallylsulfonate (SMAS) were prepared in aqueous solution using potassium persulfate (KPS) as the initiator. The effects of reaction conditions (e.g., monomer concentration, initiator concentration, monomer fractions and pH, reaction temperature and times, etc.) on the copolymerization were also studied. The results showed that higher conversion could be obtained under suitable conditions (see Figs. 1–5). The copolymers were characterized by IR and NMR spectroscopy. The ratios of infrared absorbances at 1585 cm^{-1} (carboxyl absorption) and 1048 cm^{-1} (sulfonic group absorption) were used to determine the composition of poly(MA-co-SMAS). The reactivity ratios were calculated by Kelen-Tudos method and Fineman-Ross method. Both the chemical analysis and the scanning electron micrographs showed that the copolymer has an excellent antiscaling effect on calcium carbonate.

INTRODUCTION

Water-soluble polymers have shown many properties lending themselves to a wide variety of applications. Copolymers containing carboxylic and sulfonic groups are excellent antiscaling agents.^{1–3} In our continuing investigation we now report the synthesis, characterization, and properties of the copolymer of *cis*-butenedioic acid with sodium methallylsulfonate. In the synthesis, the effects of reaction conditions on copolymerization were studied. The reactivity ratios were calculated. In addition, we report the antiscaling ability of the copolymer's.

EXPERIMENTAL

Materials

Cis-butenedioic acid, pure grade, was recrystallized twice from water and vacuum dried to constant weight. Sodium methallylsulfonate was purified by recrystallization with 95% alcohol and vacuum dried to constant weight. Potassium persulfate (KPS) was recrystallized from water. Sodium hydroxide (chemically pure) was used as purchased.

Procedure

The copolymerization of MA with SMAS was conducted in aqueous solution using potassium persulfate as initiator. *Cis*-butenedioic acid (M_1) and sodium methallylsulfonate (M_2) were dissolved in water. The cooled aqueous solution was neutralized with NaOH aq. to adjust the pH. The inert gas (N_2) was bubbled through while stirring. The initiator (KPS) was introduced into the reaction vessel. At the end of the reaction, the resulting copolymer was precipitated by pouring the solution into methanol or methanol-ethanol mixture, washed, and the product was purified by repeated precipitation and vacuum dried to constant weight. The copolymerization was carried out under various reaction conditions. Conversions (%) were determined gravimetrically.

Spectra

NMR spectra for poly(MA-co-SMAS) were obtained using FX-90 Q spectrometer with D_2O as solvent and TMS as the internal reference.

IR spectra were recorded with a NICOLET FT-20 SX spectrophotometer.

Molecular Weight Measurement

Vapor pressure osmometry (VPO) was utilized to estimate molecular weight (M_n) using a KNAUER VPO meter, at 37°C, NaCl as standard.

Thermogravimetric Analysis

The thermal stability of the copolymer was estimated by TGA.

Antiscaling Value (%)

The copolymer was added to the 250-mL aq. of equivalent $NaHCO_3$ and $CaCl_2$ at pH 8, and heated at 70°C for 6 h. The filtrate was titrated with EDTA.

RESULTS AND DISCUSSION

Effects of Reaction Conditions on Conversion (%)

Initiator Concentration (Fig. 1)

It was observed that higher conversion was obtained in KPS concentration, 0.075–0.10 mol/L.

Reaction Temperature (Fig. 2)

The conversion increased with increasing reaction temperature; however, the temperature above 85°C showed much decrement.

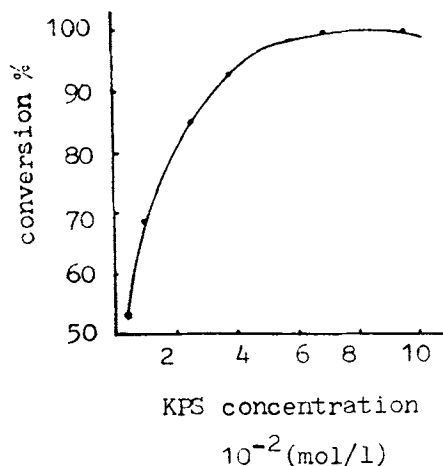


Fig. 1. Effect of KPS concentration on conversion (%). SMAS/MA = 1 mol, pH = 4.3, copolymerization at 80°C, 4 h.

Monomer Total Concentration (Fig. 3)

The conversion increased with increasing the total concentration of monomer. The 2.5 mol/L (C) is the best in experimental concentration range.

Monomer Fraction in Feed (Fig. 4)

The copolymerization of MA with SMAS was studied in the range of 0.2–0.7 MA mole fraction. Figure 4 shows the conversion of copolymerization increase with increasing MA mole fraction in the feed. The conversion for 0.7 mole fraction is always over 98% after the initial half hour. As was expected the various monomer ratios showed different reaction rate toward copolymerization. The more MA mole fraction, the higher the conversion.

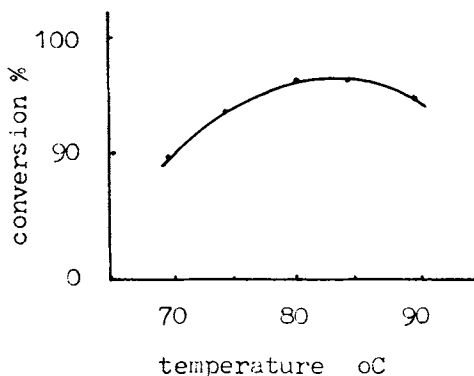


Fig. 2. Copolymerization temperature conversion curves. SMAS/MA = 1 mol, KPS concentration 0.05 mol/L, pH = 4.3, copolymerization 4 h.

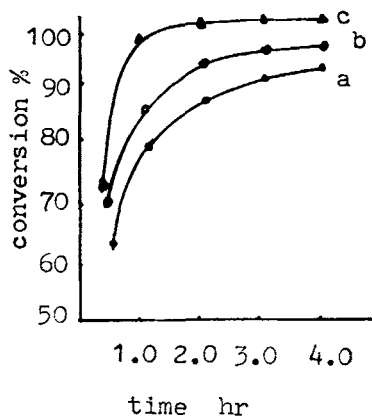
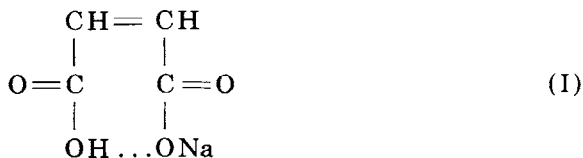


Fig. 3. Relationships of copolymerization times and conversion at various total monomer concentration (M_{tot}). M_{tot} : (a) 1.6, (b) 2.0, (c) 2.5 mol/L. SMAS/MA = 1 mol, KPS/ M_{tot} = 0.025 mol, at pH = 4.3, 80°C.

pH (Fig. 5)

At pH 4.3, the predominance structure (I) occurs through cyclization by intramolecular hydrogen bond, which would have raised the conjugative stability⁴ of free radicals.



Thus, an actual increase in conversion of copolymerization with SMAS could be anticipated.

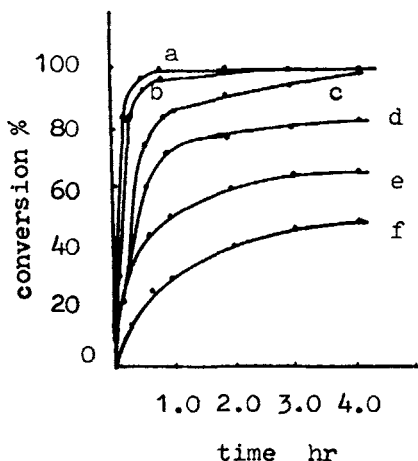


Fig. 4. Relationships of conversion and monomer (MA) mole fraction. M_{tot} = 2.5 mol/L, KPS concentration = 0.075 mol/L, pH = 4.3, 80°C.

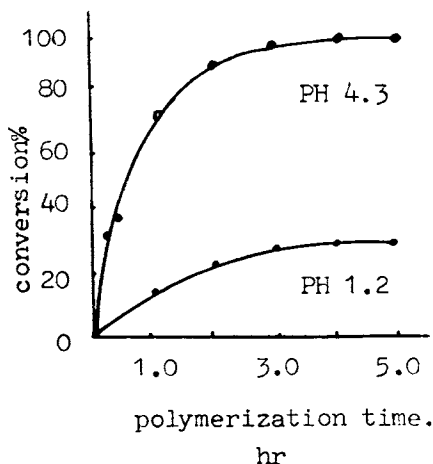


Fig. 5. Effect of pH on conversion. SMAS/MA = 1 mol, KPS concentration = 0.1 mol/L, at 70°C.

In summary, to obtain satisfactory result, the best reaction conditions are

Total monomer concentration: 2.5 mol/L

Monomer (MA) mole fraction: 0.5–0.7

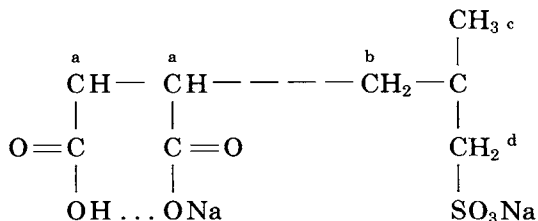
Initiator concentration: 0.075–0.10 mol/L

Reaction temperature: 80°C

pH = 4.3, reaction times: 4 h.

¹H-NMR [Fig. 6(a)] and ¹³C-NMR [Fig. 6(b)] Spectra

In the ¹H-NMR spectrum, the distinct peak assignments for copolymers are



The chemical shift values (ppm) are

$$\begin{array}{ll}
 \text{Ha} = 3.2 & \text{Hb} = 1.9 \\
 \text{Hc} = 1.3 & \text{Hd} = 2.6
 \end{array}$$

We have obtained ¹³C-NMR spectrum with DEPT method. As explained in the spectrum, the copolymer constitution is random (see also reactivity ratios).

IR Spectra (Fig. 7)

In the spectra, the constituent comonomer units show distinct characteristic peaks. For MA, carboxyl absorption is at 1585 cm⁻¹; for sulfonate it is at 1048 cm⁻¹.

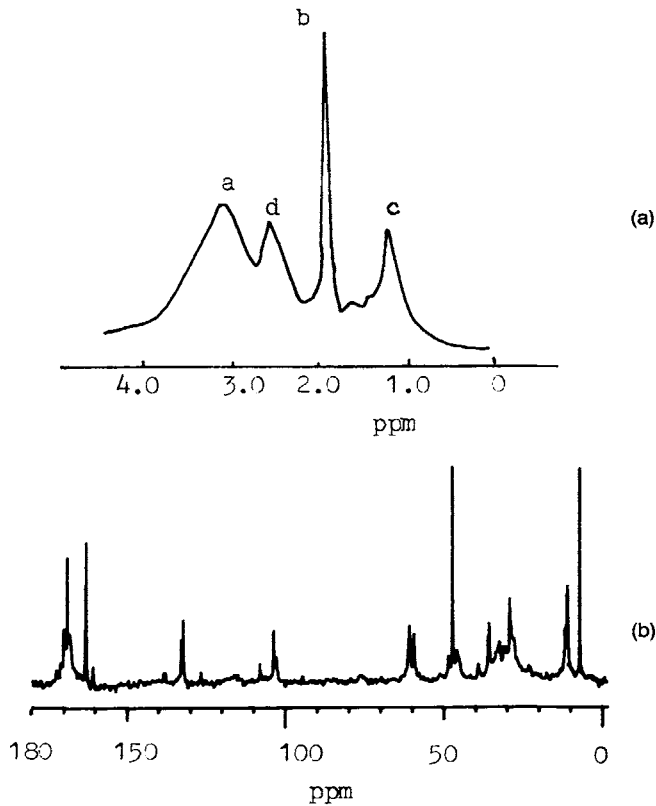


Fig. 6. NMR spectrum for poly(MA-co-SMAS). (a) $^1\text{H-NMR}$, (b) $^{13}\text{C-NMR}$.

The copolymer composition was determined from the ratio of characteristic peaks. Absorbance peak ratios A_{1585}/A_{1048} were determined for a series of copolymer and plotted as a function of $X_{\text{MA}}/X_{\text{SMAS}}$ (Fig. 8).

The results (Fig. 8) may be represented mathematically

$$A_{1585}/A_{1048} = 0.864Y + 1.255$$

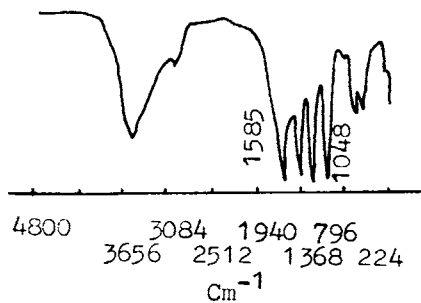


Fig. 7. IR spectrum for poly(MA-co-SMAS).

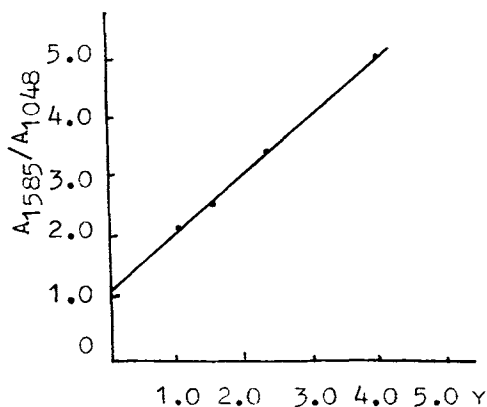


Fig. 8. Plot for poly(MA-co-SMAS) derived from infrared absorbance 1585 cm^{-1} (carboxyl) and 1048 cm^{-1} (sulpho).

where 0.864 is derived from the slope of the line while 1.255 is derived from the intercept. $Y = X_{\text{MA}}/X_{\text{SMAS}}$ represent the ratio of copolymer composition.

Thus, the mole fraction of each unit in the copolymer is easily determined.

Reactivity Ratio

Copolymerization for different monomer feed ratios (M_1/M_2) were carried out in an aqueous solution at 80°C with free-radical initiator (KPS). The conversion was in all cases restricted within 10%. The Fineman-Ross method⁵ and Kelen-Tudos method⁶ were employed to calculate the reactivity ratios.

The Fineman-Ross copolymerization equation is

$$\frac{F}{f}(f-1) = r_1 \frac{F^2}{f} - r_2$$

where $F = (M_1)/(M_2)$, and $f = d(M_1)/d(M_2)$.

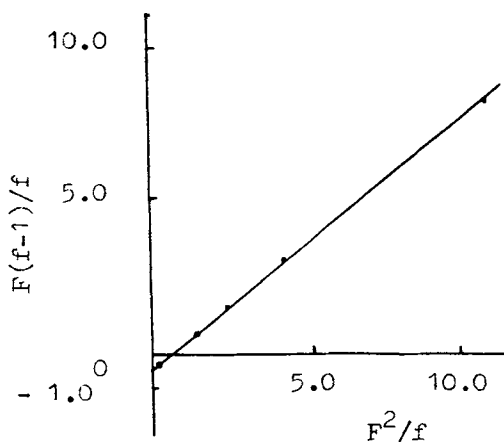


Fig. 9. Determination of reactivity ratios for the copolymerization of MA with SMAS by the Fineman-Ross method.

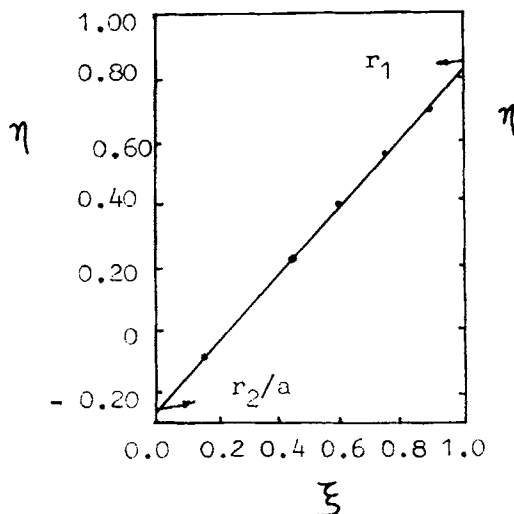


Fig. 10. Kelen-Tudos plot for the determination of reactivity ratios for the copolymerization of MA with SMAS. $a = 1.6578$.

Figure 9 is the Fineman-Ross plot for MA (M_1) and SMAS (M_2). The reactivity ratio r_1 was determined to be 0.84 from the slope of the line and $r_2 = 0.39$ from the intercept.

The Kelen-Tudos equation

$$\eta = (r_1 + r_2/a)\xi - r_2/a \quad (1)$$

where $\eta = G/(a + F)$ and $\xi = F/(a + F)$. In this expression,

$$F = \frac{(m_1/m_2)^2}{dm_1/dm_2} \quad \text{and} \quad G = \frac{m_1/m_2}{dm_1/dm_2} \left(\frac{dm_1}{dm_2} - 1 \right)$$

parameter a is obtained from $a = \sqrt{F_m F_M}$, where F_m and F_M are the lowest and highest F from the experimental data. By plotting η versus ξ according to the linear equation (1), we obtain directly r_2 (i.e., r_2/a) and r_1 from the intercepts (Fig. 10) at $\xi = 0$ and $\xi = 1$, respectively.

A plot of the data according to the Kelen-Tudos method is shown in Figure 10, and graphical evaluation yields reactivity ratios $r_1 = 0.85$ and $r_2 = 0.40$.

TABLE I
Reactivity Ratios for the Copolymerization of MA (M_1) with SMAS (M_2)

Method	r_1	r_2	$r_1 r_2$
Fineman-Ross	0.84	0.39	0.33
Kelen-Tudos	0.85	0.40	0.34

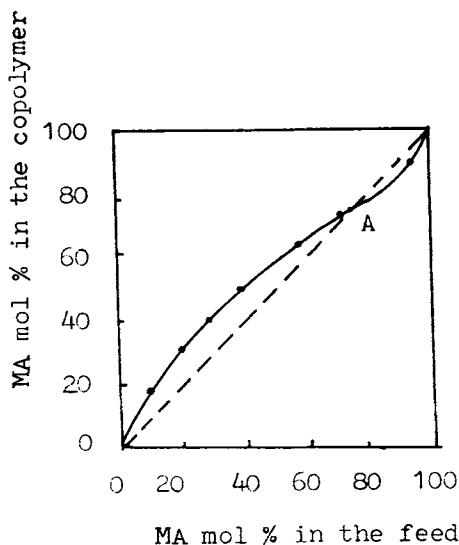


Fig. 11. Relationship between composition of monomer and copolymer.

A comparison of reactivity ratios is given in Table I.

The calculated reactivity ratios with both methods were found to be in good agreement.

The copolymer composition as a function of feed composition for the copolymerization of MA with SMAS is shown in Figure 11. The curve was derived from the copolymerization using the experimentally determined Kelen-Tudos reactivity ratios.

Because the reactivity ratios are $r_1 < 1$, $r_2 < 1$, the copolymer composition is different from monomer composition in the feed (Fig. 11). From the reactivity ratios, it can be seen that the copolymers are generally random in nature, possessing a slight alternating tendency.

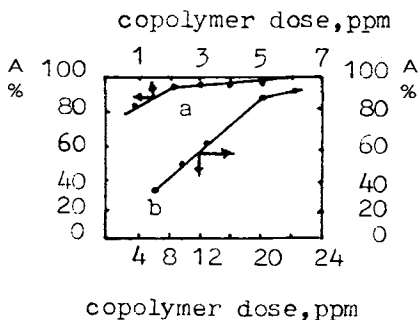
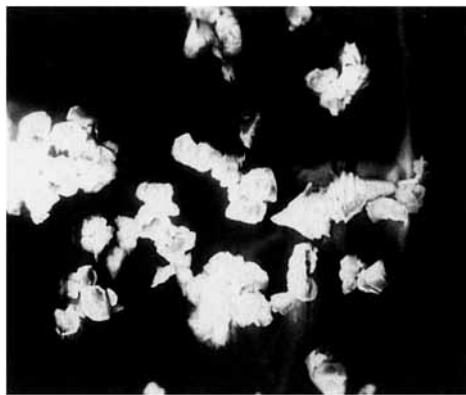


Fig. 12. Antiscalting effect of copolymer; pH = 8.5, heat at 70°C, 6 h: (a) Ca²⁺ 200 ppm; (b) Ca²⁺ 200 ppm and PO₄³⁻ 10 ppm.



(A)



(B)

Fig. 13. SEM graphs for defective lattice of calcium carbonate (A) and CaCO_3 crystal (B).

Thermogravimetric Analysis

The copolymers began to lose their weight at 190°C , and $T_{1/2} = 545^\circ\text{C}$. Sample weight 5.5869 mg, in N_2 .

Antiscaling Value (A %)

It was found that the copolymer ($M_n = 3000$) added to the synthetic hard water reduces scaling due to calcium carbonate as well as calcium phosphate (Fig. 12).

TABLE II
Effect of pH on Antiscaling Value (A %)*

pH	7.0	7.5	8.0	8.5	9.0
A %	100	100	100	100	55

* Ca^{2+} 200 ppm, heated at 70°C , 6 h, poly(MA-co-SMAS) dose 2 ppm.

TABLE III
Effect of Temperature on Antiscaling Value (A %)^a

Temperature (°C)	60	70	80	90
A %	100	100	94	82

^a Ca²⁺ 200 ppm, pH 8.5, 6 h, poly(MA-co-SMAS) dose 2 ppm.

The scanning electron micrographs showed that the defective lattice of calcium carbonate had risen due to the presence of the copolymer (Fig. 13).

Both the chemical analysis and SEM graphs showed that the copolymer had excellent antiscaling ability for calcium carbonate and phosphate. It was found that the copolymer is more effective in the temperature range of 60–70°C and pH 7.0–8.0 (Table II and III).

References

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Received March 20, 1989

Accepted October 2, 1989