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Copolymerization of methyl 2-acetamidoacrylate and styrene in the presence of stannic chloride

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Abstract

Continuous variation method in UV revealed that methyl *N*-acetylaminoacrylate (MNA) and $SnCl_4$ formed the 1:1 complex. The copolymerization of MNA with styrene in tetrahydrofuran was carried out at 50 °C in the presence of $SnCl_4$. The resulting monomer reactivity ratios decreased with an increasing concentration of $SnCl_4$ added. This finding suggests that $SnCl_4$ participates in the propagation step of the copolymerization. Therefore, the copolymerization was analyzed by assuming terpolymerization of free MNA (M_1), complexed MNA (M_2), and styrene (M_3). The absolute copolymerization parameters were obtained as follows: $k_{11}/k_{12} = 0.165$, $k_{11}/k_{13} = 3.04$, $k_{22}/k_{21} = 0.32$, $k_{22}/k_{23} = 0.103$, $k_{33}/k_{31} = 0.058$, $k_{33}/k_{32} = 0.001$, $Q_1 = 6.03$, $e_1 = 0.52$, $Q_2 = 88.57$, and $e_2 = 2.23$. The complexed MNA is more reactive to polymer radicals with free MNA and styrene as the terminal unit than the free MNA. Very small values of k_{22}/k_{23} and k_{33}/k_{32} suggests that the copolymerization of the complexed MNA and styrene proceeds alternatingly.

Keywords: Methyl 2-acetamidoacrylate; Styrene; Stannic chloride; Copolymerization; Metal complex; Terpolymerization; Monomer reactivity ratios

1. Introduction

It is well known that polar vinyl monomers such as methyl methacrylate and acrylonitrile easily form a complex with Lewis acid and that the complex copolymerizes alternatingly with conjugated vinyl monomers such as styrene [1]. The copolymerization of monomers having positive and negative *e*-values has been also reported in the presence of a small amount of metal salts [2–5]. In these cases, monomer reactivity ratios varied with the quantity of the metal salt added.

In the preceding paper [6], the polymerization of methyl 2-acetamidoacrylate (*N*-acetylaminoacrylate, abbreviated MNA) which has amide and oxycarbonyl groups was kinetically investigated in water and organic solvents. It was concluded from copolymerization parameters obtained that the acetylamino group does not have polarizing action but significant resonance effect.

The complexation of methyl MNA with a metal salt is expected to be superior to that of methyl acrylate because of a synergistic effect of two functional groups (amido and oxycarbonyl). In practice, stability constants for complexes of poly(*N*-acetamidoacrylic acid) with various divalent metal ions are larger than those for poly(acrylic acid) [7].

This article describes the copolymerization of MNA with styrene (St) in the presence of stannic chloride ($SnCl_4$). If MNA forms a complex with $SnCl_4$, this system can be dealt with by a random terpolymerization of

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free MNA, complexed MNA and St. At first, it is tried to confirm the formation of the complex by means of UV spectrometer. In the next place, the copolymerization of MNA and St was carried out in the presence of $SnCl_4$ of various concentrations. The monomer reactivity ratios obtained are the apparent values because these changes with the concentrations of $SnCl_4$ added. The absolute monomer reactivity ratios were evaluated from the apparent ones according to the composition equation for three component system.

2. Experimental

2-acetamidoacrylic acid was prepared by refluxing a benzene solution of pyruvic acid and acetamide [8]. MNA was prepared according to the procedure of Bueno et al. [9]: An acetone solution of 2-acetamidoacrylic acid and methyl iodide was refluxed and then cooled. The precipitate was isolated by filtration and extracted with chloroform. After removal of chloroform by distillation under reduced pressure, MNA was recrystallized from hexane. Yield 87%, mp 50–52 °C (Ref. [10] 50–52 °C).

The equilibrium constant for the MNA–$SnCl_4$ complex was evaluated according to the Benesi–Hildebrand equation [11]. UV spectra were recorded on a Shimadzu UV-3000 spectrometer.

Comonomer, initiator (2,2′-azobisisobutyronitrile (AIBN)), and solvents were commercially available and purified by standard methods prior to use. Stannic chloride was of special grade and used without further purification.

The copolymerization of MNA with St was carried out in the presence or absence of $SnCl_4$. The required amount of monomers, initiator, $SnCl_4$ and solvent (tetrahydrofuran (THF)) were placed in a tube, cooled in cooling bath, degassed by successive freeze-pump-thaw cycles, and sealed under vacuum. The sealed tube was placed in a thermostat maintained at 50 °C. After a given time, copolymerization were stopped by pouring the reaction mixture onto a large excess of petroleum. The resulting copolymer was filtered off, dried under reduced pressure, and weighed. The yield was up to 10%. The copolymer composition was determined by elemental analysis. Monomer reactivity ratios were calculated to the method of Kelen–Tüdös [12].

3. Results and discussion

When MNA forms a complex with $SnCl_4$, the copolymerization of MNA with St in the presence of $SnCl_4$ may be dealt with as the terpolymerization of free MNA (M_1), complexed MNA (M_2), and St (M_3). Therefore, in order to confirm the formation of the complex, continuous variation method in UV spectra was carried out for the MNA–$SnCl_4$ system. Measurements were made in dioxane at a constant wave length (278 nm). Fig. 1 shows continuous variation plot for the MNA–$SnCl_4$ system. Maximum absorption appeared at $[MNA]/[SnCl_4] = 1$. This shows the formation of the 1:1 complex.

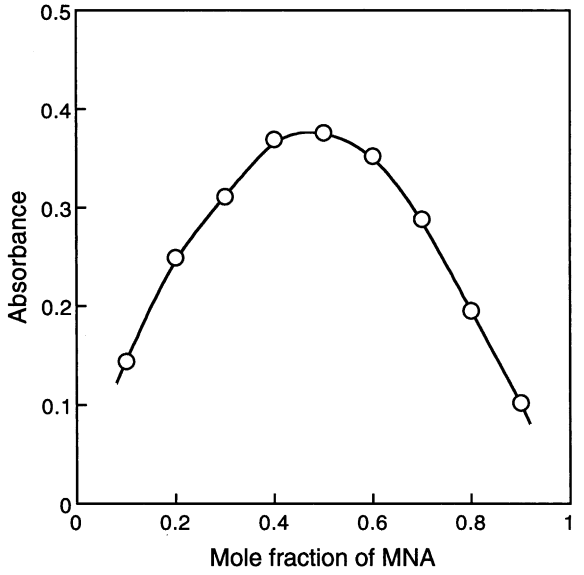

Fig. 1. Continuous variation method in UV spectra for the MNA–$SnCl_4$ system. $[MNA] + [SnCl_4] = 0.05$ mol/l; Solvent, Chloroform; Wavelength, 278 nm.

The equilibrium constant (K) can be evaluated according to the Benesi–Hildebrand equation (Eq. (1))

$$\frac{[SnCl_4]l}{d} = \frac{1}{K\varepsilon}\frac{1}{[MNA]} + \frac{1}{\varepsilon} \tag{1}$$

where l, d, and ε express light path length, absorbance, and molar extinction coefficient, respectively. Fig. 2 shows Benesi–Hildebrand plot for the MNA–$SnCl_4$ system. The equilibrium constant and molar extinction coefficient of the complex were determined as $K = 6.81$ and $\varepsilon = 6.2 \times 10^3$ from the slope and intercept of the straight line, respectively.

The copolymerization of MNA with St in the presence of $SnCl_4$ was carried out at 50 °C in THF. The molar ratios of $SnCl_4$ to MNA were in the range of 0–0.05. Table 1 shows relationship between molar percentages of MNA in the feed monomer and in the resulting copolymer. The content of MNA in the copolymer increases with an increase in the content of MNA in the feed and a decrease in the amount of $SnCl_4$ added. Fig. 3 shows examples of Kelen–Tüdös plots. Monomer reactivity ratios were evaluated from values at $\xi = 0$ and $\xi = 1$. Fig. 4 shows typical monomer–copolymer composition curves for the copolymerization

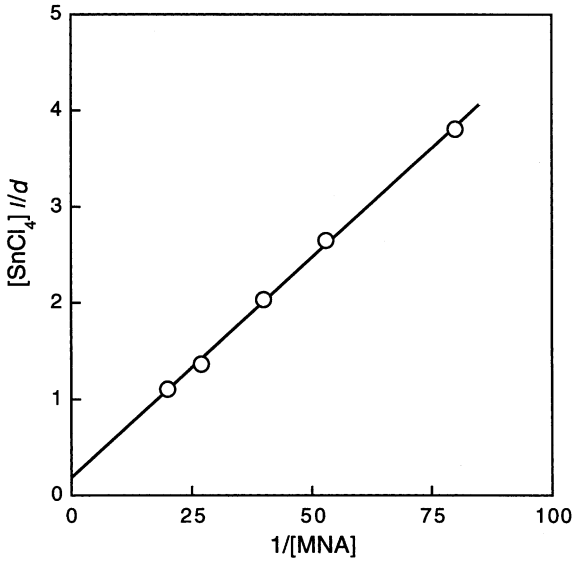

Fig. 2. Benesi–Hildebrand plot for the MNA–$SnCl_4$ system. Solvent, Chloroform; Wavelength, 282 nm.

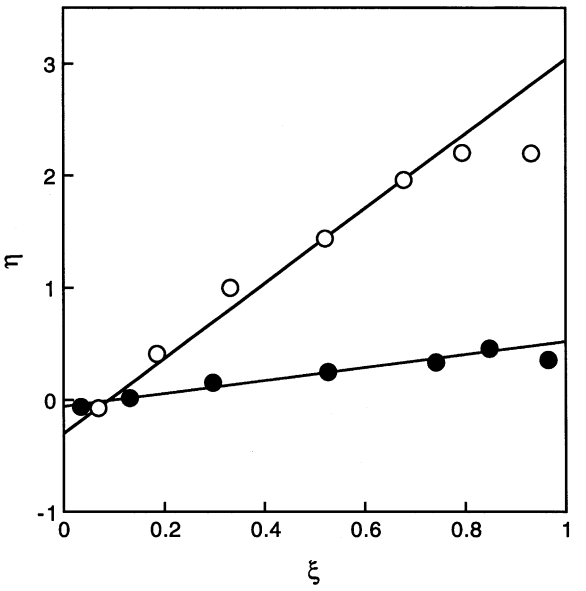

Fig. 3. Kelen–Tüdös plots for the copolymerization of MNA with St in the presence or absence of $SnCl_4$. (○): $[SnCl_4]/[MNA] = 0$, (●): $[SnCl_4]/[MNA] = 0.05$.

of MNA with St. In the Kelen–Tüdös plots, the experimental points of [MNA]/[St] in the feed = 86.8/13.2 deviate from the straight lines for both systems ($x = 0$ and $x = 0.05$). However, experimental points give good correlation with theoretical curves of monomer–copolymer relationship. Table 2 lists apparent monomer reactivity ratios determined on the basis of the data shown in Table 1.

As can be seen from Table 2, both monomer reactivity ratios (r_1 and r_2) decrease with an increasing concentration of $SnCl_4$. This finding suggests that $SnCl_4$ participates in the propagation step of the copolymerization (probably as the complex of MNA and $SnCl_4$). Therefore the copolymerization of MNA with St in the presence of $SnCl_4$ can be dealt with as random terpolymerization of free MNA (M_1), MNA complexed with $SnCl_4$ (M_2), and St (M_3).

There are nine possible chain propagations in the random terpolymerization as follows. The elementary reaction is

$$M_i^{\bullet} + M_j \rightarrow M_j^{\bullet} \quad i = 1,2,3 \quad j = 1,2,3 \tag{2}$$

the reaction rate being $k_{ij}[M_i^{\bullet}][M_j]$.

The probability of the addition of St to the polymer radical with free or complexed MNA unit as the terminal group is given by

$$P_{ab} = \left[(k_{13}[M_1^{\bullet}][M_3] + k_{23}[M_2^{\bullet}][M_3])/(k_{11}[M_1^{\bullet}][M_1] + k_{12}[M_1^{\bullet}][M_2] + k_{21}[M_2^{\bullet}][M_1] + k_{22}[M_2^{\bullet}][M_2] + k_{13}[M_1^{\bullet}][M_3] + k_{23}[M_2^{\bullet}][M_3])\right] \tag{3}$$

Table 1
Monomer–copolymer composition relationship for the copolymerization of MNA and St in the presence of $SnCl_4$[a]

MNA in feed monomer (mol%)	MNA unit in the copolymer (mol%)						
	x[b] = 0	0.005	0.01	0.02	0.03	0.04	0.05
10.1	46.9	46.7	44.5	44.0	43.9	44.7	44.4
20.9	61.3	57.1	54.6	53.2	51.4	50.4	50.9
32.7	71.1	64.9	62.3	58.3	56.5	54.7	55.6
45.4	76.7	73.3	68.2	63.8	60.5	58.5	58.2
59.3	83.9	79.8	75.6	69.1	66.8	63.3	62.3
70.5	88.4	83.6	81.1	76.1	71.2	71.0	69.5
86.8	94.3	89.9	87.0	84.5	82.0	81.5	77.4

[a] [MNA] + [St] = 2.67 mol/l, [AIBN] = 5×10^{-3} mol/l.
[b] $x = [SnCl_4]/[MNA]$.

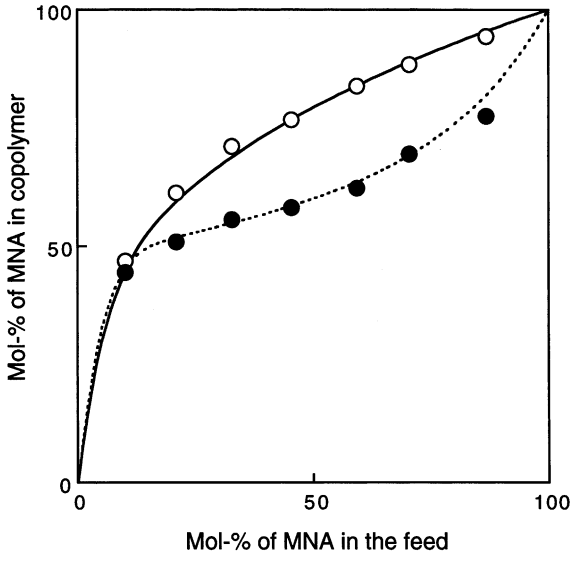

Fig. 4. Monomer–copolymer composition curves for the copolymerization of MNA with St in the presence or absence of $SnCl_4$. (○): $[SnCl_4]/[MNA] = 0$, (●): $[SnCl_4]/[MNA] = 0.05$.

Table 2
Apparent monomer reactivity ratios for the copolymerization of MNA and St in the presence of $SnCl_4$

$[SnCl_4]/[MNA]$	r_1	r_2	$r_1 \times r_2$
0	3.04	0.058	0.176
0.005	2.01	0.045	0.090
0.01	1.45	0.037	0.054
0.02	0.91	0.027	0.025
0.03	0.69	0.021	0.014
0.04	0.55	0.017	0.009
0.05	0.52	0.015	0.008

Two assumptions are made for obtaining a conventional form of the composition equation. (1) Migration of $SnCl_4$ between MNA monomer and the polymer radical with the MNA unit at the terminal position easily takes place (Eq. (4)). (2) MNA–$SnCl_4$ complex goes essentially to completion (complexation constant $(K = 6.81)$ reveals that over 90% of $SnCl_4$ added forms the complex). Therefore, the concentration of the complexed monomer may be considered the concentration of $SnCl_4$.

$$M_1^{\bullet} + M_2 \rightleftharpoons M_1 + M_2^{\bullet} \tag{4}$$

$$K' \text{ (equilibrium constant)} = \frac{[M_1][M_2^{\bullet}]}{[M_1^{\bullet}][M_2]}$$

When $[M_1] + [M_2]$ and the ratio $[M_2]/[M_t]$ are replaced by $[M_t]$ and x, respectively, Eq. (5) can be derived.

$$P_{ab} = \Big[(\{k_{13}(1-x) + k_{23}K'x\}[M_3]) \Big/ (\{k_{11}(1-x)^2 + k_{12}(1-x)x + k_{21}K'(1-x)x + k_{22}K'x^2\}[M_t] + \{k_{13}(1-x) + k_{23}K'x\}[M_3])\Big] \tag{5}$$

x is much less than unity. Therefore, Eq. (5) is rewritten into Eq. (6).

$$P_{ab} = \frac{(k_{13} + k_{23}K'x)[M_3]}{(k_{11} + k_{12}x + k_{21}K'x + k_{22}K'x^2)[M_t] + (k_{13} + k_{23}K'x)[M_3]} \tag{6}$$

Therefore

$$P_{ab} = \frac{[M_3]}{r_1([M_1] + [M_2]) + [M_3]} \tag{7}$$

where

$$r_1 = \frac{\dfrac{k_{11}}{k_{13}} + \dfrac{k_{12} + k_{21}K'}{k_{13}}x + \dfrac{k_{22}K'}{k_{13}}x^2}{1 + \dfrac{k_{23}K'}{k_{13}}x} \tag{8}$$

The another probability (P_{ba}) of the propagation reactions is given in the same way.

$$P_{ba} = \frac{k_{31}[M_3^{\bullet}][M_1] + k_{32}[M_3^{\bullet}][M_2]}{k_{31}[M_3^{\bullet}][M_1] + k_{32}[M_3^{\bullet}][M_2] + k_{33}[M_3^{\bullet}][M_3]}$$
$$P_{ba} = \frac{[M_1] + [M_2]}{([M_1] + [M_2]) + r_2[M_3]} \tag{9}$$

where

$$r_2 = \frac{\dfrac{k_{33}}{k_{31}}}{1 + \dfrac{k_{32}}{k_{31}}x} \tag{10}$$

The composition equation for the terpolymerization is represented as follows.

$$\frac{d[M_1] + d[M_2]}{d[M_3]} = \frac{P_{ba}}{P_{ab}} = \frac{[M_1] + [M_2]}{[M_3]} \frac{r_1([M_1] + [M_2]) + [M_3]}{([M_1] + [M_2]) + r_2[M_3]} \tag{11}$$

Figs. 5 and 6 show monomer reactivity ratio as a function of $[SnCl_4]/[MNA]$. The coefficients which satisfied Eqs. (8) and (10) were determined using the nonlinear least squares method (Syntex method). The resulting equations are

$$r_1 = \frac{3.04 + 0.76x + 11.33x^2}{1 + 110.30x} \tag{12}$$

$$r_2 = \frac{0.058}{1 + 58.00x} \tag{13}$$

From $k_{11}/k_{13} = 3.04$ and $k_{33}/k_{31} = 0.058$, Q_1 and e_1 values for free MNA monomer were calculated as 6.03

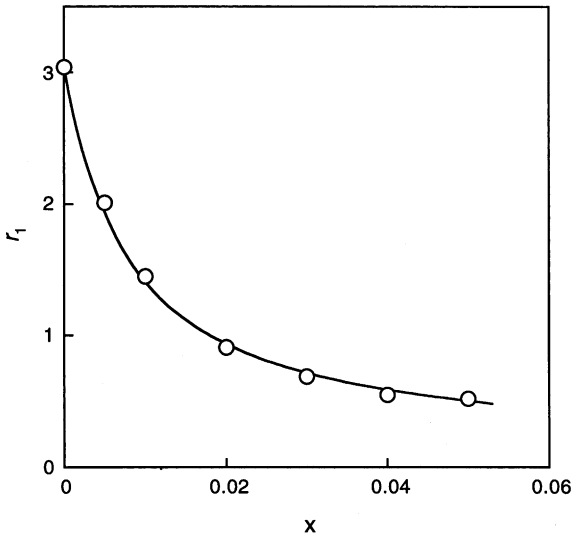

Fig. 5. Plot of r_1 against x.

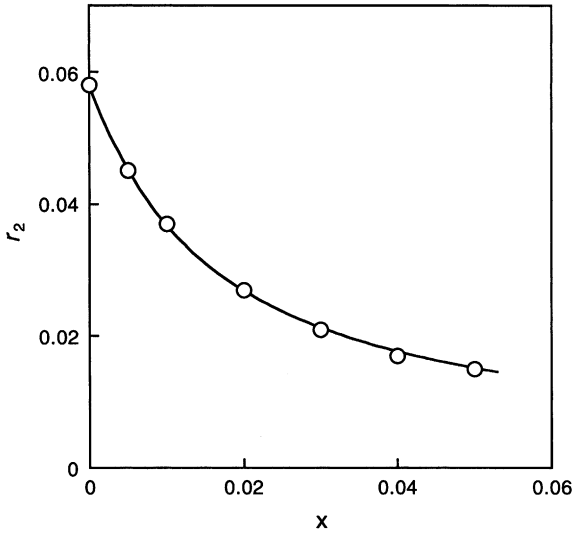

Fig. 6. Plot of r_2 against x.

and 0.52, respectively, by assuming $Q_3 = 1.0$ and $e_3 = -0.8$ for St. $k_{22}/k_{23} = (k_{22}K'/k_{13})/(k_{23}K'/k_{13})$ is evaluated as $11.33/110.30 = 0.103$ and $k_{33}/k_{32} = (k_{33}/\ k_{31})/(k_{32}/k_{31})$ as $0.058/58.00 = 0.001$. Q_2 and e_2 values for complexed MNA monomer were calculated as 88.57 and 2.23 from the values of k_{22}/k_{23} and k_{33}/k_{32}, respectively. Other absolute monomer reactivity ratios can be calculated by using the obtained Q and e values. The resulting copolymerization parameters are summarized in Tables 3 and 4.

The magnitude of the rate constants for addition of respective monomers to respective polymer radicals are in the following order:

Table 3
Q and e values for free and complexed MNA

Monomer	Q	e
Free MNA (M_1)	6.03	0.52
Complexed MNA (M_2)	88.57	2.23
St (M_3)	1.0	−0.8

Table 4
Absolute monomer reactivity ratios for the random terpolymerization of free MNA (M_1), complexed MNA (M_2), and St (M_3)

k_{11}/k_{12}	0.165
k_{11}/k_{13}	3.04
k_{12}/k_{13}	18.42
k_{22}/k_{21}	0.320
k_{22}/k_{23}	0.103
k_{23}/k_{21}	3.15
k_{33}/k_{31}	0.058
k_{33}/k_{32}	0.001
k_{32}/k_{31}	58.00

$$k_{13} < k_{11} < k_{12} \quad k_{22} < k_{21} < k_{23} \quad k_{33} < k_{31} < k_{32}$$

The complexed MNA is more reactive to polymer radicals with the free MNA and St terminal units: The complexed monomer adds to polystyryl radical about 60 times as fast as the free monomer. The both values of k_{22}/k_{23} and k_{33}/k_{32} are small. This means that the copolymerization of the complexed MNA and St proceeds alternatingly.

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