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POLYMERIZABLE TAUTOMERS. X. RADICAL POLYMERIZATION AND COPOLYMERIZATION OF ETHYL 3-OXO-4-PENTENOATE IN THE PRESENCE OF COBALT(II) ACETATE

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ABSTRACT

The radical polymerization of ethyl 3-oxo-4-pentenoate (EAA) was kinetically investigated at 50°C in the presence of cobalt(II) acetate. The rate of polymerization is proportional to the 0.51th and 3.12th powers of concentrations of cobalt(II) acetate and monomer, respectively. The following polymerization mechanism is assumed on the basis of the kinetic results. A cobalt(II) ion forms a complex with three molecules of monomer, and polymerization is initiated by a radical which is generated by interaction of the complex and free monomer. The apparent activation energy was 56.7 kJ/mol. The value obtained was smaller than that for AIBN-catalyzed polymerization. Radical copolymerization of EAA (M_1) and styrene (M_2) was carried out at 50°C in the presence of cobalt(II) acetate. The monomer reactivity ratio r_1 increases with increasing concentration of cobalt(II) acetate, while r_2 is independent of the concen-

tration of the metal salt. This implies the participation of a metal complex in the propagation step of the copolymerization.

INTRODUCTION

There are many reports on the redox polymerization by a system of an organic compound with an active hydrogen and a transition metal. Metal chelates of acetylacetone and ethyl acetacetate, which have an active hydrogen, are also known to initiate the radical polymerization of vinyl compounds and aldehydes [1-5].

In a series of polymerizable tautomers, the authors have reported that ethyl 3-oxo-4-pentenoate (ethyl acryloylacetate, abbreviated EAA) exhibits the coexistence of two tautomers, the ketonic and enolic forms, and its tautomeric equilibrium shifts with the polarity of the solvents [6]. The copolymerizability of EAA also depends on the solvents [7].

EAA has a β-ketoester group, i.e., the active hydrogen. If the metal complex of EAA is subjected to a redox reaction and to radical formation, EAA can be radically polymerized without any radical catalyst. That is, EAA may behave as both catalyst and monomer.

This paper describes the kinetics of radical polymerization of EAA in the presence of cobalt(II) acetate without any radical catalyst.

EXPERIMENTAL

Ethyl 3-oxo-4-pentenoate (EAA) was prepared according to a method previously reported [6]: bp 78-80°C (2.4 kPa). Cobalt(II) acetate was a special reagent grade from Kanto Chemical Co. and used without further purification. Styrene and the other agents were commercially available and purified by standard methods prior to use.

Polymerization and copolymerization in methanol were conducted at 50°C in tubes sealed under vacuum. The reaction was homogeneous. After a given time, the reaction mixture was brought together in a large excess of methanol containing a trace of hydrochloric acid. The resulting polymer precipitate was filtered off, dried under reduced pressure, and weighed. The rate of polymerization was determined gravimetrically, and the copolymer composition was found by elemental analysis. The monomer reactivity ratios were calculated by the Kelen-Tüdös method [8].

RESULTS AND DISCUSSION

The polymerization of EAA was carried out at 50°C in the presence of cobalt(II) acetate without any radical catalyst. Methanol was used as a solvent, taking into account the solubility of the monomer and the metal salt. Methanol is one of precipitants of the polymer. However, the polymerization proceeded homogeneously under the conditions studied. This means that PEAA is soluble in a mixture of monomer and methanol when the monomer occupies a certain proportion in the

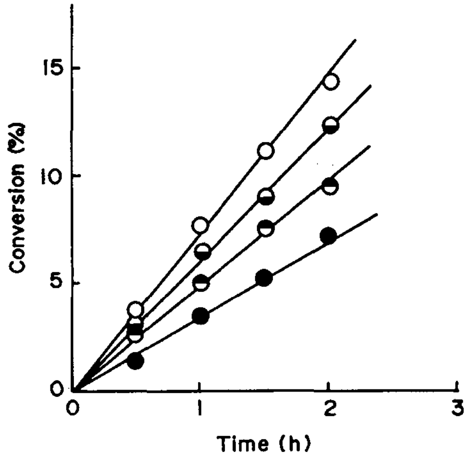


FIG. 1. Time-conversion curves for EAA polymerization. [EAA] = 2.07 mol/L. [$Co(OAc)_2$] = 2.07 × 10^{-2} (○), 1.55 × 10^{-2} (◒), 1.04 × 10^{-2} (◓), and 0.52 × 10^{-2} (●) mol/L. 50°C.

reaction mixture. That is to say, the reaction mixture is a good solvent for the polymer.

Figure 1 shows time-conversion curves for the polymerization of EAA with constant concentration of monomer and various concentrations of the cobalt salt. There is no induction period between reaction time and conversion, and the time-course is linear to a conversion of 10% and above. Figure 2 shows the dependence of the polymerization rate (R_p) on the concentration of cobalt(II) acetate

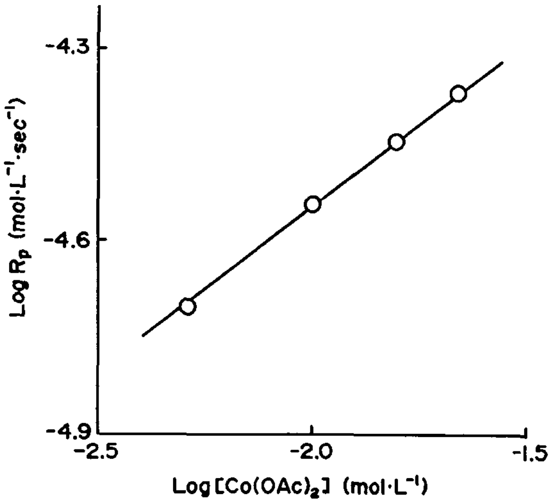


FIG. 2. Relationship between polymerization rate and concentration of cobalt(II) acetate. [EAA] = 2.07 mol/L. 50°C.

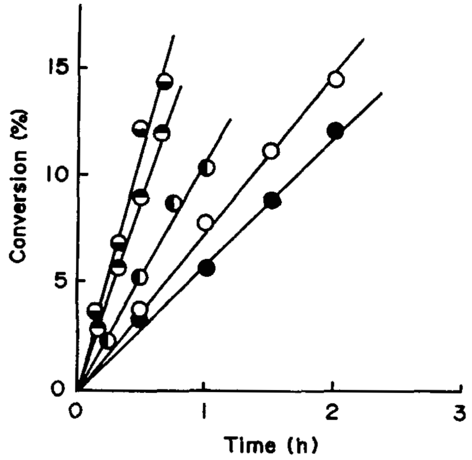


FIG. 3. Time-conversion curves for the EAA polymerization. [Co(OAc)$_2$] = 2.07 × 10^{-2} mol/L. [EAA] = 3.62 (◒), 3.01 (◓), 2.41 (◐), 2.07 (○), and 1.81 (●) mol/L. 50°C.

[Co(OAc)$_2$]. The slope of the straight line indicates that the polymerization rate is proportional to the 0.51th power of the cobalt salt.

Figure 3 illustrates plots of time versus conversion for the polymerization of EAA with various EAA concentrations, and the rate of polymerization is evaluated from the slope of the straight lines. The reaction order with respect to EAA concentration was found to be 3.12 from the slope in Fig. 4. Consequently, the rate equation is expressed as

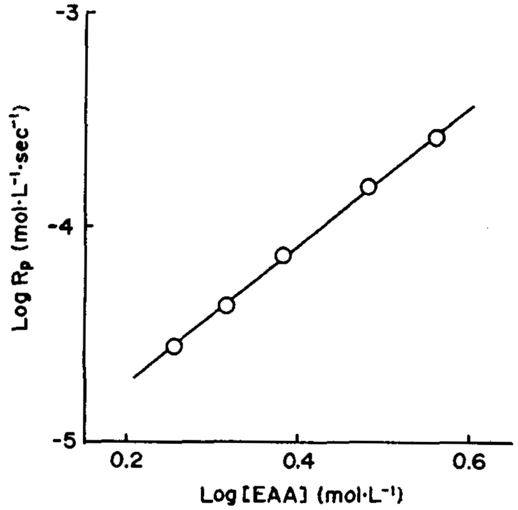
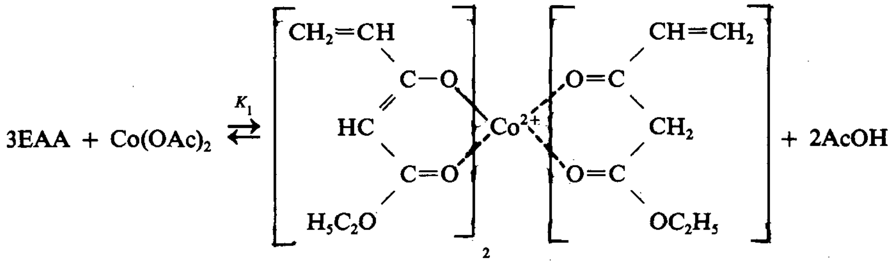


FIG. 4. Relationship between polymerization rate and monomer concentration. [Co(OAc)$_2$] = 2.07 × 10^{-2} mol/L. 50°C.

$$R_p = k[\mathrm{Co(OAc)_2}]^{0.51}[\mathrm{EAA}]^{3.12}$$

The rate of polymerization is approximately proportional to the square root of concentration of cobalt(II) acetate. This suggests the participation of cobalt(II) ion in the initiation step (probably in the form of the complex with EAA) and of two propagating radicals in the termination step. Furthermore, this is also suggestive of a radical mechanism because of obedience to the square root rule. The polymerization rate is a function of a higher order with respect to the concentration of EAA. This finding reveals that EAA takes part in both initiation and propagation steps.

EAA forms a complex with various metal ions, of course with cobalt ion, because of a ketoester group as a substituent. The coordination number of cobalt(II) ion is usually six. It is therefore assumed that the cobalt(II) ion coordinates three molecules of EAA.



[Co·EAA$_3$]

Elementary reactions of the polymerization may be expressed as follows.

Initiation: $\mathrm{Co\cdot EAA_3 + EAA \overset{K_2}{\rightleftarrows} Co\cdot EAA_4}$

$\mathrm{Co\cdot EAA_4 \xrightarrow{k_i} CO\cdot EAA_3 + EAA\cdot}$

(or $\mathrm{Co\cdot EAA_2 + EAA_2\cdot}$)

Propagation: $\mathrm{EAA\cdot + EAA \xrightarrow{k_p} EAA\cdot}$

Termination: $\mathrm{2EAA\cdot \xrightarrow{k_t} P}$ or 2P

In the initiation, the dissociation of the complex Co·EAA$_4$ is accompanied by the formation of either a monomeric or a dimeric EAA radical. No precipitation of metallic cobalt from solution is presumed because there is no reduction from the divalent ion to the metal. Therefore it is speculated that the reduced cobalt reverts rapidly to the divalent ion by electron migration to a proton because of the very unstable monovalent ion.

Assuming that the equilibrium constants (K_1 and K_2) are very small, the rate of initiation (R_i) is

$$\begin{aligned} R_i &= k_i\,[\mathrm{Co\cdot EAA_4}] = k_i\cdot K_2\,[\mathrm{Co\cdot EAA_3}][\mathrm{EAA}] \\ &= k_i\cdot K_1\cdot K_2\,[\mathrm{Co(OAc)_2}][\mathrm{EAA}]^4 \end{aligned}$$

By applying the steady-state approximation to the active intermediate, the following rate equation is derived.

$$R_p = k_p\,[\mathrm{EAA}\cdot][\mathrm{EAA}]$$
$$= k_p\left(\frac{k_1\cdot K_1\cdot K_2}{k_t}\right)^{0.5}[\mathrm{Co(OAc)_2}]^{0.5}[\mathrm{EAA}]^3$$

The derived rate equation satisfies the kinetic results obtained. However, it is not obvious from the kinetic results whether the EAA-cobalt(II) acetate complex ($\mathrm{Co\cdot EAA_3}$) participates in propagation and termination steps of the polymerization or not.

Arnett and Mendelsohn [9] proposed that the mechanism for vinyl polymerization by a metal acetylacetonate includes the reaction of the formation of a ligand radical, which is responsible for the initiation step, by homolytic dissociation of the metal-oxygen bond. The assumption of introducing a ligand molecule into a polymer was confirmed by Kastning et al. [2]. Otsu et al. [10] reported the participation of monomer in the initiation step of radical polymerization of methyl methacrylate by copper(II) acetacetate because the reaction rate is proportional to the 1.4th power of the monomer concentration. The mechanism of polymerization of EAA in the presence of cobalt(II) acetate is similar to that for the polymerization of methyl methacrylate by copper(II) acetacetate proposed by Otsu et al.

Variation of the logarithms of the polymerization rate with the reciprocal temperature was utilized to obtain the apparent activation energies. The activation energies for polymerization in the presence of cobalt(II) acetate and for the AIBN-catalyzed polymerization were evaluated as 56.7 and 92.2 kJ/mol, respectively, on the basis of the results in Fig. 5. The smaller value of the activation energy for the former suggests that polymerization in the presence of cobalt(II) acetate is initiated by a redox reaction between a ligand molecule and a chelating metal ion.

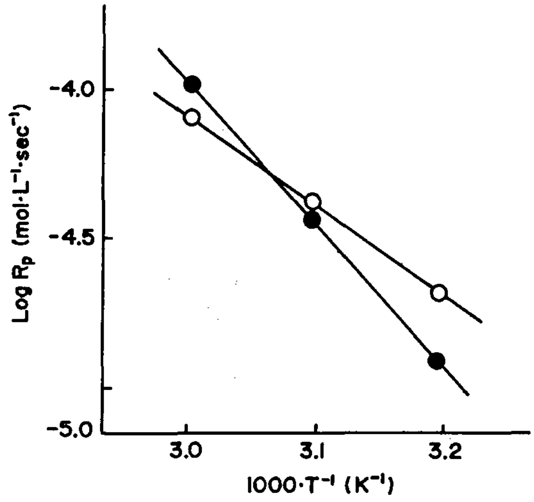


FIG. 5. Arrhenius plots for the polymerization of EAA catalyzed by the cobalt complex (○) and by AIBN (●).

TABLE 1. Monomer-Copolymer Composition for the Copolymerization of EAA (M_1) and Styrene (M_2) in the Presence of Cobalt(II) Acetate[a]

Mol% of M_1 in the feed	Mol% of M_1 in the copolymer					
	$x^b = 1 \times 10^{-4}$	2×10^{-4}	5×10^{-4}	1×10^{-3}	2×10^{-3}	1×10^{-2}
12.8	25.3	28.6	28.7	27.7	26.1	28.8
26.2	40.2	38.7	40.4	41.4	38.4	42.0
35.6	43.5	46.7	50.1	46.0	45.0	50.5
45.3	46.5	49.7	48.1	52.3	54.4	62.1
55.4	54.4	54.9	56.8	56.3	57.0	71.3
65.9	58.8	59.6	62.5	66.1	66.3	75.9
79.8	69.6	69.2	71.3	73.7	77.4	86.2

[a] [EEA] + [styrene] = 4 mL, [methanol] = 3 mL, 50°C.

[b] $x = [Co(OAc)_2]/[EEA]$ (mole ratio).

Copolymerization of EAA (M_1) and styrene (M_2) in methanol was carried out at 50°C in the presence of various amounts of cobalt(II) acetate. The conversion was up to 5%. At such a low conversion, copolymerization proceeded homogeneously. The monomer-copolymer composition relationships are listed in Table 1. Contents of the monomeric unit of EAA in a copolymer have a tendency to increase with an increase in the concentration of cobalt(II) acetate.

Table 2 shows monomer reactivity ratios determined on the basis of the data shown in Table 1 according to the Kelen-Tüdős method [8] together with those for the copolymerization catalyzed by AIBN. Monomer reactivity ratio r_1 increases with an increase in the concentration of cobalt salt, while r_2 is independent of the metal salt. This finding implies the participation of the metal complex of monomer ($Co \cdot EAA_3$) in the propagation step of the copolymerization.

TABLE 2. Monomer Reactivity Ratios for the EAA (M_1)/Styrene (M_2) System

Additive or initiator		Solvent	r_1	r_2	Reference
$Co(OAc)_2$:	$x = 1 \times 10^{-4}$	Methanol	0.37	0.30	
	$x = 2 \times 10^{-4}$	Methanol	0.40	0.28	
	$x = 5 \times 10^{-4}$	Methanol	0.41	0.25	
	$x = 1 \times 10^{-3}$	Methanol	0.55	0.27	
	$x = 2 \times 10^{-3}$	Methanol	0.67	0.34	
	$x = 1 \times 10^{-2}$	Methanol	1.41	0.32	
AIBN		Methanol	0.66	0.15	7
		Carbon tetrachloride	2.68	0.16	7
		Acetonitrile	0.57	0.22	7

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