Radical Polymerizations of Vinyl Monomers in the Presence of α-Ethylsulfenyl Acrylonitrile

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ABSTRACT

Radical polymerizations of styrene, methyl methacrylate, and acrylonitrile were carried out at 60°C in the presence of α-ethylsulfenyl acrylonitrile (α-ESAN). The rate of polymerization was found to be reduced by the addition of α-ESAN, and induction periods were observed when a large amount of α-ESAN was added to the systems. The chain transfer constant of α-ESAN was determined to be 2.0 and 17 for the polymerizations of styrene and methyl methacrylate, respectively. The Q_{tr} and e_{tr} values of α-ESAN were evaluated as 4.9 and -1.9, respectively. The presence of chromium(II) acetate and α-ESAN results in enhancement of α-ESAN activity as a retarder. From these results and ESR measurements, a mechanism of chain transfer is discussed.

INTRODUCTION

Capto-dative substituted compounds have recently been investigated in such fields as organic synthesis, biochemistry, and physical chemistry [1, 2]. Capto-dative substituted olefins have been of special in-

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terest as good reagents for the generation of stable radicals since
they possess opposite substituent polarization and can trap any
radical regardless of its polarity [3, 4]. At present, however, little is
known about the ability of such olefins as inhibitors or retarders in
radical polymerization. The study of this ability is of interest not only
for the development of new radical stabilizers but also for the elucida-
tion of the factor controlling the reactivity of a propagating polymer
radical.

In this paper we deal with the reactivity of such capto-dative sub-
stituted olefins as α-ethylsulfenyl acrylonitrile (α-ESAN) as retarders
in the radical polymerization of monomers with various polarities,
namely styrene, methyl methacrylate, and acrylonitrile. The effect
of such additives as chromium(II) acetate, which has been known to
stabilize a radical by a one-electron transfer reaction [5], on the rate
of polymerization has also studied for the change of reactivity of α-
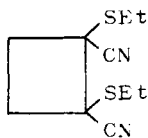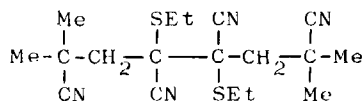ESAN.

EXPERIMENTAL

Materials

α-Ethylsulfenyl acrylonitrile was prepared by the reaction of α-
chloroacrylonitrile and ethyl mercaptan [6]; yield 35%, bp 50°C/10
mmHg, m/e(M^+) 113. ^{1}H-NMR (TMS, neat): δ 1.30 ppm (3H, t), 2.87
(2H, q), 5.90 (1H, d), 6.04 (1H, d). The purity was checked by gas
chromatography.

Commercially available styrene, methyl methacrylate, and acrylo-
nitrile were purified by the usual methods. Azobisiosbutyronitrile
(AIBN) was used after recrystallizations from ethanol and chloroform.
Chromium(II) acetate was synthesized by the reaction of chromium di-
chloride and anhydrous sodium acetate in a dry box [7].

A cyclic dimer of α-ESAN (I) and an adduct dimer of α-ESAN and
isobutylonitrile (II) were prepared as follows:

$$\text{Me-}\underset{\underset{CN}{|}}{\overset{\overset{Me}{|}}{C}}\text{-CH}_2\text{-}\underset{\underset{CN}{|}}{\overset{\overset{SEt}{|}}{C}}\text{---}\underset{\underset{SEt}{|}}{\overset{\overset{CN}{|}}{C}}\text{-CH}_2\text{-}\underset{\underset{Me}{|}}{\overset{\overset{CN}{|}}{C}}\text{-Me}$$

I   II

Heating of α-ESAN in bulk at 60°C for 5 h gave (I) in 85% yield
based on α-ESAN. Isolation by TLC using a mixture of petroleum
ether and diethyl ether (4:1 volume ratio) as a developing solvent
gave two products: cis (R_f = 0.55) and trans (R_f = 0.68) forms;

m/e(M$^+$) 226. ^{1}H-NMR (TMS in CDCl$_3$) for the cis form: δ 1.28 ppm (6H, t), 2.76 (4H, q), 2.10-3.00 (4H, m); for the trans form: δ 1.29 ppm (6H, t), 2.87 (4H, q), 1.70-3.10 (4H, m).

Analysis: Found for the cis form: C, 53.16%; H, 6.21; N, 12.21. Found for the trans form: C, 53.30%; H, 6.18; N, 12.21. Calculated for (I): C, 53.10%; H, 6.19; N, 12.39.

A mixture of both isomers was used for the reactions.

A mixture of α-ESAN (1.54 mL) and AIBN (1.08 g) was heated in benzene (20 mL) for 26 h at 60°C and then the reaction mixture was cooled to around 7°C. A white powder (II) was precipitated in 45.2% yield (1.06 g). Recrystallization of this product from benzene gave white needles (mp 160-161 C) and colorless plates (mp 175-176 C), which are the meso form and the racemate [8]; m/e(M + 1)$^+$ 363. ^{1}H-NMR (TMS in CDCl$_3$) for the meso form: δ1.37 (6H, t), 1.59 (6H, s), 2.11 (2H, d), 2.34 (2H, d), 3.17-3.28 (4H, m); for the racemate: δ1.37 ppm (6H, t), 1.59 (6H, s), 1.66 (6H, s), 2.50 (2H, d), 3.38 (2H, broad s), 3.22-3.33 (4H, m).

Analysis: Found for the meso form: C, 59.57%; H, 7.23; N, 15.52. Found for the racemate: C, 59.40%; H, 7.06; N, 15.63. Calculated for (II): C, 59.67%; H, 7.18; N, 15.47.

For the thermal decomposition experiment, a mixture of both isomers was used.

Measurements

The ESR spectra were recorded on a JEOL JES-FE2XG spectrometer equipped with 100 kc/s modulation at 100°C. Constant temperature was attained with a JEOL ES-DVT1 temperature controller. The JEOL ES-9835 data system was used for spectrum simulation.

The ^{1}H-NMR spectra were measured on either a Hitachi R-24B, 60 MHz, or a JEOL GX-400, 400 MHz, spectrometer at room temperature. For measurement of the dimerization of α-ESAN, dioxane was used as the internal standard for relative intensity of absorption.

Polymerization

The rate of polymerization was measured by means of dilatometry at 60°C. After degassed, the monomer and α-ESAN were mixed with AIBN, and the solution was transferred into a dilatometer under vacuum. For the polymerization of acrylonitrile, dimethylformamide was used as solvent.

RESULTS AND DISCUSSION

Effect of α-ESAN

Figures 1, 2, and 3 show the time-conversion curves for the polymerizations of styrene, methyl methacrylate, and acrylonitrile in the presence or absence of α-ESAN. In all cases it is clear that the rate of polymerizations was reduced by the addition of α-ESAN, and induction periods were observed when a large amount of α-ESAN was added to the systems. The polymers thus obtained were homopolymers and α-ESAN did not copolymerize with these monomers, so α-ESAN acts only a retarder, and its activity is large in the polymerization of acrylonitrile and small in that of styrene.

The chain transfer constant of α-ESAN (C_{tr}) was determined by [9]

$$\frac{1}{R_p} - \frac{1}{R_{p_0}} = \frac{C_{tr}}{R_i} \frac{[\alpha\text{-ESAN}]}{[\text{monomer}]} \tag{1}$$

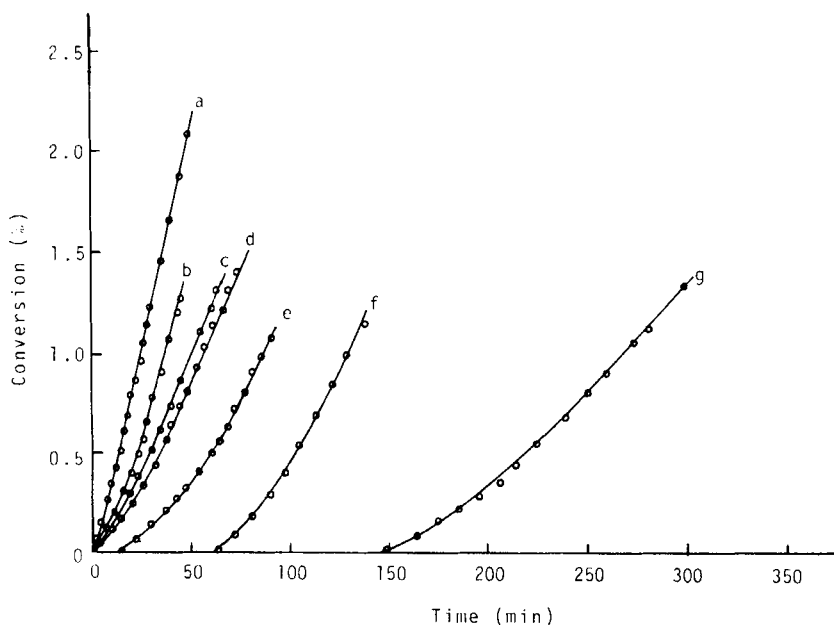FIG. 1. Polymerizations of styrene in the presence of α-ESAN. [AIBN], 5.0 mmol/L; [α-ESAN], (a) 0, (b) 0.80, (c) 1.6, (d) 2.2, (e) 3.5, (f) 6.7, (g) 14 mmol/L.
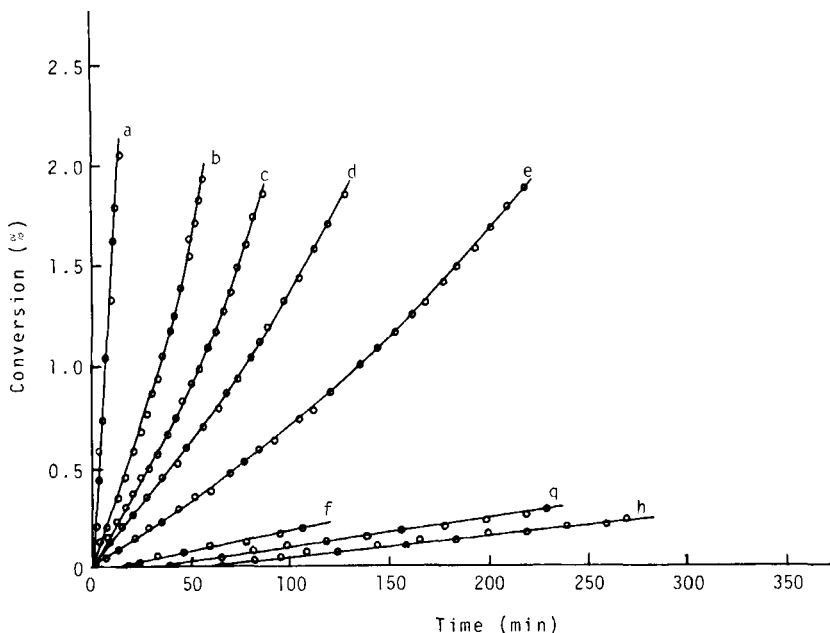
FIG. 2. Polymerizations of methyl methacrylate in the presence of α-ESAN. [AIBN], 5.0 mmol/L; [α-ESAN], (a) 0, (b) 0.37, (c) 0.56, (d) 1.2, (e) 1.7, (f) 3.4, (g) 6.7, (h) 14 mmol/L.

where R_p is the rate of polymerization as determined from the initial slope at low concentrations of α-ESAN in Figs. 1 and 2, R_{p_0} is the rate of polymerization in the absence of α-ESAN, and R_i indicates the rate of initiation. In accordance with this relation, a plot of $(1/R_p) - (1/R_{p_0})$ against [α-ESAN]/[monomer] was found to be linear, as shown in Fig. 4, suggesting the production of a dead radical by the chain transfer of a propagating radical toward an α-ESAN since Eq. (1) is valid in such a case. Based on the slopes in Fig. 4 and R_i values in the literature [10], C_{tr} was determined to be 2.0 and 17 for the polymerizations of styrene and methyl methacrylate, respectively. From the C_{tr} values obtained Q_{tr} and e_{tr} of α-ESAN in the theory of Fuhrman and Mesrobian [11] were calculated to be 4.9 and -1.9, respectively. Although it is not suitable for exact discussion because of experimental error, a negative value of e_{tr} supports a higher C_{tr} value for methyl methacrylate than for styrene.
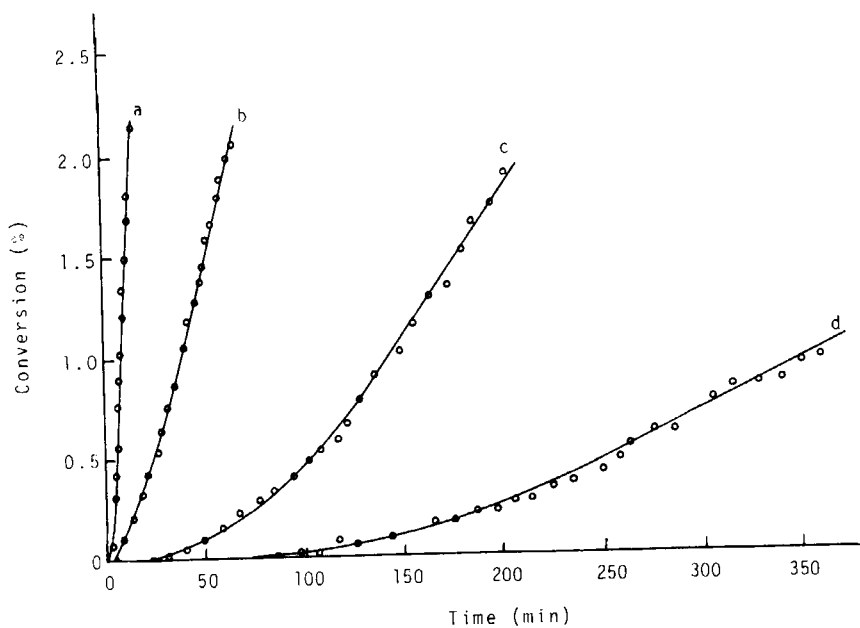
FIG. 3. Polymerizations of acrylonitrile in the presence of α-ESAN. [AIBN], 5.0 mmol/L; [α-ESAN], (a) 0, (b) 0.58, (c) 2.5, (d) 7.2 mmol/L.
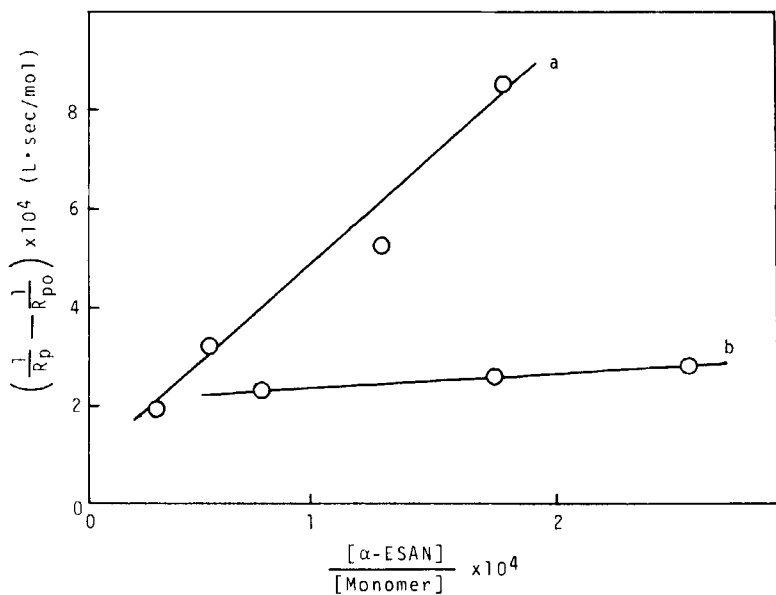

FIG. 4. Determination of chain transfer constants of α-ESAN in the polymerizations of methyl methacrylate (a) and styrene (b).
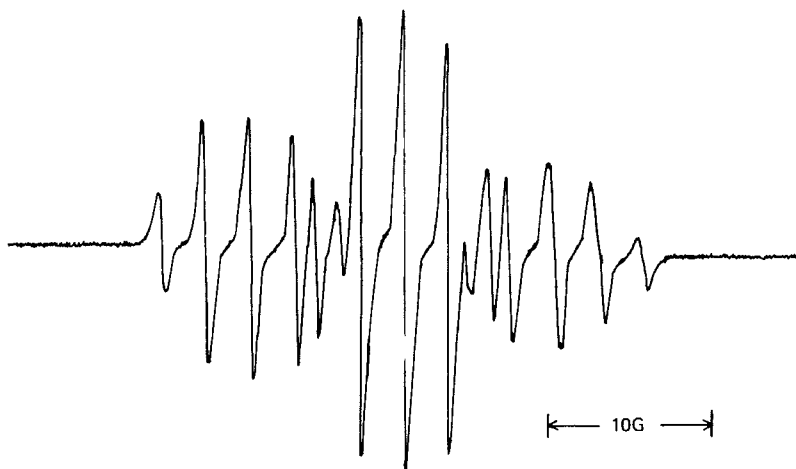
FIG. 5. ESR spectrum generated from the reaction of α-ESAN and AIBN in dioxane at 100°C. [α-ESAN], 2.1 mol/L; [AIBN], 0.6 mol/L.

ESR spectra were measured to reveal the chain transfer reaction mechanism. Figure 5 shows the ESR spectrum generated from the reaction of α-ESAN and AIBN in dioxane at 100°C. For comparison, Adducts (I) and (II) were prepared by separate experiments, and Radical Intermediates (III) and (IV) were developed by thermal decomposition:
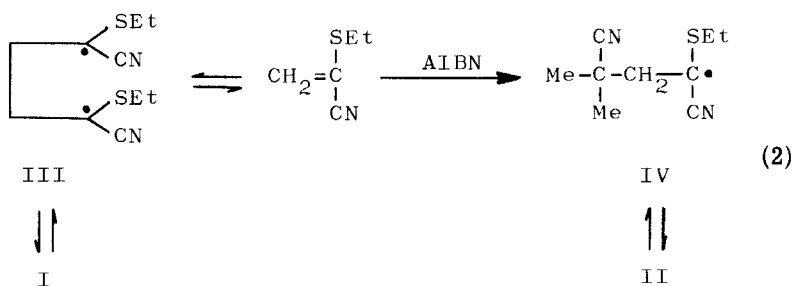
The ESR spectral data thus obtained are listed in Table 1. A comparison of the ESR spectrum in Fig. 5 with that of (III) or (IV) shows that the spectrum in Fig. 5 consists of a mixture of the Radical Species (III) and (IV), and spectrum simulation suggests that the latter participates over 90%. Therefore, the following reaction (Eq. 3) may be most important chain transfer reaction, and the production of Radical V seems to stabilize and deactivate a propagating radical.

TABLE 1. ESR Spectral Data of the Radicals III and IV[a]

Radical	Hyperfine coupling constants (G)		
	$a_{H(\beta)}$	$a_{H(\gamma)}$	a_N
III	9.10	2.70	2.70
IV	8.95	2.43	2.70

[a]Conditions of measurements: [I] = 1.1 mol/L, [II] = 0.65 mol/L, in dioxane at 100°C.
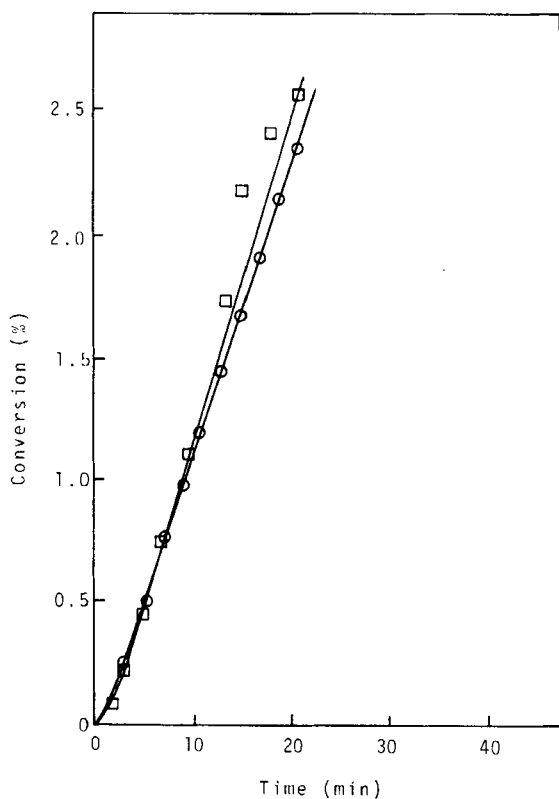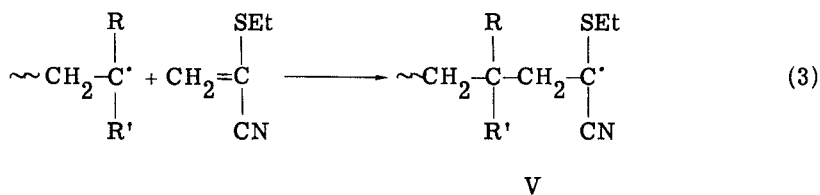
FIG. 6. Polymerizations of acrylonitrile in dimethylformamide in the presence (○) or absence (□) of the cyclic dimer (I). [AIBN], 5.0 mmol/L; [I], 2.9 mmol/L; [acrylonitrile], 3.79 mol/L.

$$\sim CH_2\text{-}\underset{\underset{R'}{|}}{\overset{\overset{R}{|}}{C}}{}^{\cdot} + CH_2{=}\underset{\underset{CN}{|}}{\overset{\overset{SEt}{|}}{C}} \longrightarrow \sim CH_2\text{-}\underset{\underset{R'}{|}}{\overset{\overset{R}{|}}{C}}\text{-}CH_2\text{-}\underset{\underset{CN}{|}}{\overset{\overset{SEt}{|}}{C}}{}^{\cdot} \qquad (3)$$

<div align="center">V</div>

The contribution of Radical Intermediate (III) to retardation has also been examined (Fig. 6), with acrylonitrile used as the monomer because of the large retarding effect of α-ESAN. Figure 6 shows that the rate of polymerization of acrylonitrile is only slightly affected by the addition of Dimer (I), even at higher concentrations of dimer expected in the polymerization system. The equilibrium constant of the dimerization and the rate constant of the reaction converting α-ESAN to (I) were determined to be 3.2 L/mol and 1.7×10^{-5} L/mol·s, respectively, by means of NMR spectroscopy. Therefore the concentration of Radical (III) is very low in the actual polymerizations, and the deactivation of propagating radicals by the attack of (III) or α-ESAN reproduced by the decomposition of (I) may be neglected compared with the contribution of the reaction represented by Eq. (3).

Effect of Chromium(II) Acetate

Gundermann and Rohrl [12] reported that a metal salt such as aluminum chloride acts as an effective catalyst for rate acceleration and for enhancement of the selectivity of the reaction of capto-dative olefins. Figure 7 shows the polymerization of styrene with AIBN in the presence of chromium(II) acetate which has been reported to stabilize a radical by a one-electron transfer reaction. It is obvious from Figure 7 that the rate of polymerization is reduced by the coexistence of α-ESAN and Cr^{II}. Because the decreasing rate of polymerization caused by the addition of only Cr^{II} is not as large (as can be seen in Curve b in Fig. 7), Cr^{II} seems to increase the activity of α-ESAN as a retarder, even if there is an interaction of Cr^{II} and dimethylformamide as was recently reported [13]. Although a detail study of the interaction between Cr^{II} and α-ESAN is now in progress, the observed effect of Cr^{II} is very interesting from the viewpoint of controlling the activity of a radical.
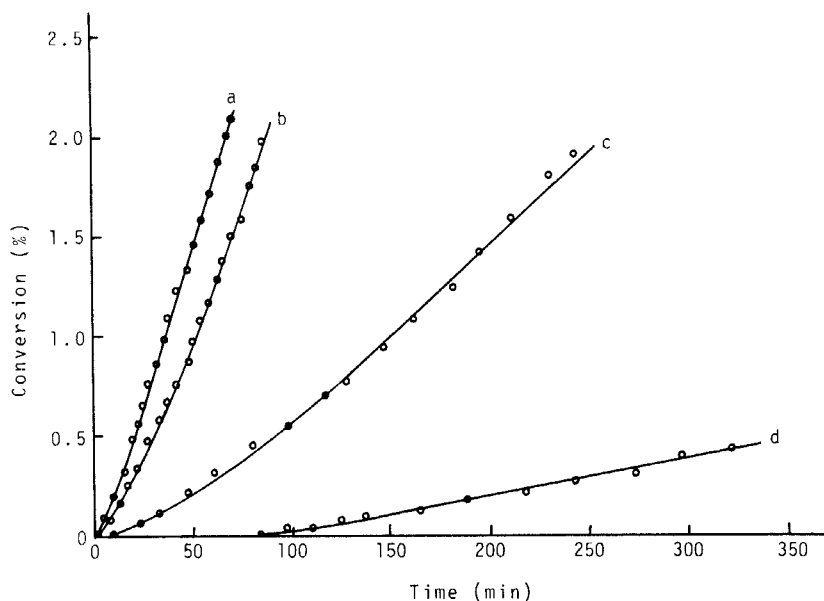
FIG. 7. Polymerizations of styrene in dimethylformamide in the presence or absence of chromium(II) acetate. [Styrene], 4.33 mol/L; [α-ESAN], 4.4 mmol/L; [Cr^{II}], 11 mmol/L; [AIBN], 5.0 mmol/L; (a) AIBN, (b) AIBN/Cr^{II}, (c) AIBN/α-ESAN, (d) AIBN/α-ESAN/Cr^{II}.

ACKNOWLEDGMENT

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