Stannous Chloride as an Effective Initiator for Copolymerization of Styrene with Maleic Anhydride

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STANNOUS CHLORIDE AS AN EFFECTIVE INITIATOR FOR COPOLYMERIZATION OF STYRENE WITH MALEIC ANHYDRIDE

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ABSTRACT

Stannous chloride was found to be an effective initiator for co-polymerization of styrene (ST) with maleic anhydride (MAH). The combination of stannous chloride as an electron donor and MAH as an electron acceptor monomer forms charge transfer complex to produce initiating radical for copolymerization of ST with MAH. The kinetics of copolymerization was studied in the temperature range of 30-60°C, and the activation energy was determined from Arrhenius plots of polymerization rate. The overall energy of activation as calculated from Arrhenius plot was found to be 23.8 kcal/mol. The rate of copolymerization (Rp) was found to be dependent on the $[SnCl_2 \cdot 2H_2O]^{0.97}$ $([MAH]+[ST])^{3.1}$.

INTRODUCTION

There have been many reports on the use of metal halides for the radical-initiated polymerization system [1-4]. For example, the radical-initiated polymerization of electron accepting monomers such as acrylonitrile and methyl methacrylate in the presence of metal halides such as zinc chloride is characterized by increased rates of polymerization. This effect has been attributed to the formation of

a complex between the electron accepting monomers and the metal halide, resulting in delocalization of the electrons in the double bond of the complexed monomers. The presence of metal halides increase the rate and comonomer content in the free radical initiated copolymerization. Although numerous papers and comprehensive reports which concern metal halides on radical polymerization has been published, no investigation withcopolymerization of electron accepting monomers initiated by metal halide alone has been made. We have found that the copolymerization of ST with MAH could be initiated and polymerized by using various initiators such as thiols, L-ascorbic acid and various reducing reagents. All these initiators acted as electron donor to the MAH and produced initiating radical. Charge transfer complex formed between these compound as electron donor and MAH as electron accepting monomer. In every systems, effective role of reducing reagent on the copolymerization of electron accepting monomers was observed. Generally, strong electron accepting monomers have no activity of homopolymerization of their own and need another comonomer for copolymerization.

We have reported various copolymerization systems [5-10] of electron accepting monomers initiated by electron donating compounds such as thiol compounds were studied on the relationship of initiation activity and electron donor ability. This paper describes the copolymerization of ST with MAH initiated by stannous chloride as one of these electron donor substances.

EXPERIMENTAL

Styrene (ST) was washed free of inhibitor with 5% NaOH solution, washed with water, distilled under vacuum, and stored at 0°C. Maleic anhydride (MAH) and fumaronitrile (FN) were recrystallized twice from dry chloroform before use. Diethyl fumarate (DEF) was commercially available and used without further purification. Citraconic acid (CA) was purified by distillation under vacuum. Stannous chloride ($SnCl_2 \cdot 2H_2O$) was recrystallized twice from dry benzene. All solvents were purified by conventional method.

Copolymerization was carried out in sealed tubes, which were stored in the absence of external light. The required amounts of MAH, ST and $SnCl_2 \cdot 2H_2O$ in dioxane were charged into a glass tube, which was then degassed under vacuum by conventional freezing and thawing techniques three times and sealed. This sealed tube was wrapped with aluminium foil to protect it from external light, and placed in a thermostat to start polymerization. After a given time, the tube was opened and its content was poured into a large amount of diethyl ether to precipitate the

copolymer. The precipitated copolymer was washed with diethyl ether and dried under vac. to constant weight. Conversions were calculated from the weight of the dried copolymer. Rates of copolymerization were obtained gravimetrically.

For the measurement of electronic spectra, a Shimadzu UV-210A spectrophotometer was used at room temperature. IR and NMR spectra were recorded by JASCO IR-S1 and Hitachi R-24B spectrophotometers, respectively.

RESULTS AND DISCUSSION

Stannous chloride can effectively initiate the copolymerization of St with MAH to give a moderate amount of alternating copolymer. Copolymerization in the absence of stannous chloride was examined to ensure that the spontaneous copolymerization rate is insignificant. The effect of oxygen on the copolymerization reaction was observed. Stannous chloride acts as an efficient initiator even in the presence of atmospheric oxygen. Atmospheric oxygen facilitates the initiation activity of stannous chloride to yield sufficient amount of the copolymer. However, excess amount of oxygen inhibits the initiation activity of stannous chloride to yield none of the copolymer. Homopolymerization of ST did not occur in the presence of stannous chloride. Copolymerization of ST with MAH occurred near room temperature in the presence of stannous chloride, the rate of polymerization being high. While in the absence of stannous chloride, the yield in the correspondence time period after initiation was much lower. However, other copolymerization systems such as copolymerization of diethyl fumarate (DEF), fumaronitrile (FN) and citraconic acid (CA) with ST by using stannous chloride as an initiator were found to yield a negligible amount of copolymers (Table 1). These accepting monomers have low ability to accept one electron from stannous chloride and generate no initiating radical. MAH is a most strong acceptor monomer among these electron accepting monomers and formed charge transfer complex with stannous chloride to produce initiation radical for the copolymerization of ST with MAH.

Copolymerization of ST with MAH occurred in the presence of stannous chloride in various solvents such as ethyl acetate, acetone, dimethyl formamide and dioxane. In dioxane, copolymerization occurred quickly to give a sufficient amount of copolymers in high yield and was quite reproducible. Therefore, almost all copolymerization was carried out in dioxane. All copolymers produced were characterized by IR, as well as NMR spectroscopy having an alternating composition.

TABLE 1. Copolymerization of Styrene with Various Monomers using $SnCl_2 \cdot 2H_2O$ as an Initiator

Monomer$_1$	Monomer$_2$	$SnCl_2 \cdot 2H_2O$ (mmol/l)	Yield (%)
MAH	ST	7.5	57.4
DEF	ST	7.5	0
CA	ST	7.5	0
FN	ST	7.5	1.6

MAH: Maleic Anhydride; DEF: Diethyl Fumarate; CA: Citraconic Acid;
FN: Fumaronitrile; ST: Styrene.
[Monomer$_1$] = [Monomer$_2$] = 1.67 mol. Solvent; Dioxane Temp. = 60°C.
Reaction time = 24 hours.

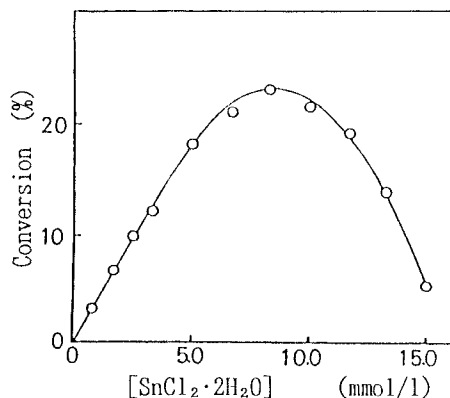**Figure 1.**   Effect of $SnCl_2 \cdot 2H_2O$ concentration on copolymerization of ST with MAH for 2 hours at 60°C. [ST]=[MAH]=1.67 mol/l. Solvent; Dioxane.

Figure 1 shows the effect of stannous chloride concentration on conversion of copolymerization. Copolymerization was carried out at equal amount of ST and MAH of 1.67mol/l in dioxane for 2 hours. Conversion of copolymerization passes through a maximum (9mmol/l) with increasing linearly in stannous chloride concentration and decreases at higher concentrations. At higher concentration, stannous chloride exhibits an inhibitory effect for the copolymerization. Retardation
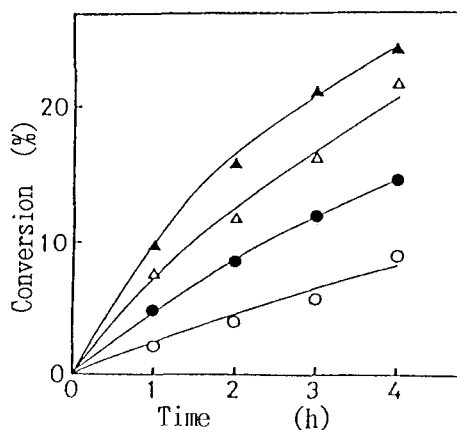
Figure 2. Time-conversion curves for copolymerization of ST with MAH initiated by $SnCl_2 \cdot 2H_2O$. [ST]=[MAH]=1.67 mol/l. Solvent; Dioxane, [$SnCl_2 \cdot 2H_2O$] = (▲) 3.33 mmol/l, (△) 2.50 mmol/l, (●) 1.67 mmol/l, (○) 0.83 mmol/l.
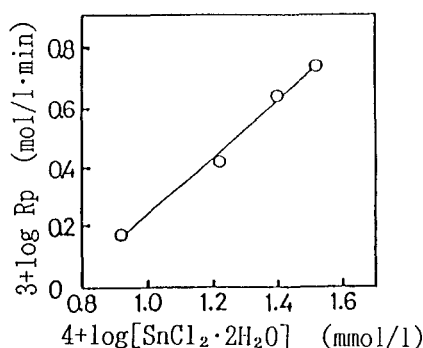

Figure 3. Effect of $SnCl_2 \cdot 2H_2O$ concentration on the rate of copolymerization.

of copolymerization is presumably due to extensive chain transfer involving growing chain ends and stannous chloride molecules.

Figure 2 shows the time-conversion curves at various concentrations of stannous chloride. The conversion of copolymerization at each stannous chloride concentration was found to be linearly proportional to the copolymerization time, however at a longer time, deviation from the normal has been observed. The rate of copolymerization (Rp) was derived from the initial slope of these conversion curves.

Figure 3 shows the relationship between the rate of copolymerization and stannous chloride concentration. At low stannous chloride concentration, Rp is
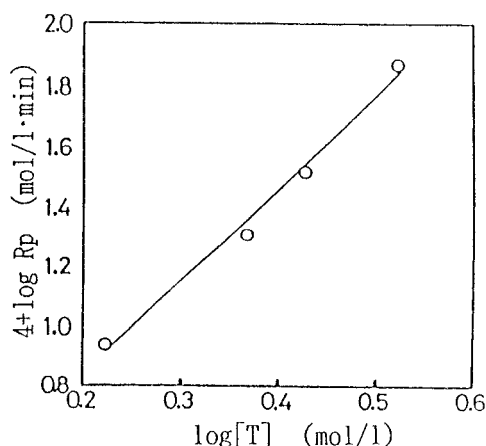
Figure 4.   Effect of total monomer concentration on copolymerization of ST with MAH initiated by $SnCl_2 \cdot 2H_2O$.

roughly proportional to the 0.97 power of stannous chloride concentration. In terms of the generally accepted kinetic interpretation these results mean that the initiation reaction involves the molecular complex of stannous chloride and is proportional to the catalyst concentration. In addition, the termination process occurs by mutual collision of the two active centers, and that the steady state approximation is reasonably well fulfilled.

The effect of total monomer concentration ([T]=[ST]+[MAH]) on the rate of copolymerization was studied. Copolymerizations were carried out with stannous chloride of 8.33 mmol at equal monomer concentrations and 60°C for 2 hours. Copolymerization reaction occurred from total monomer concentration of 1.4 mol/l and higher concentration copolymer conversion increased with increasing total monomer concentration. The conversion of copolymerization at each total monomer concentration was found to be linearly proportional to the copolymerization time, but at higher total monomer concentration, deviation from the normal has been observed. The rate of copolymerization was found to increase linearly with increasing total monomer concentration. Under the condition [ST]=[MAH]=[T]/2, where [T] is the total monomer concentration, the plots of Rp vs.   total monomer concentration are linear, passing through the origin (Figure 4) showing that the order with respect to [T] is 3.1. This result shows that the monomer involved in the initiation reaction.
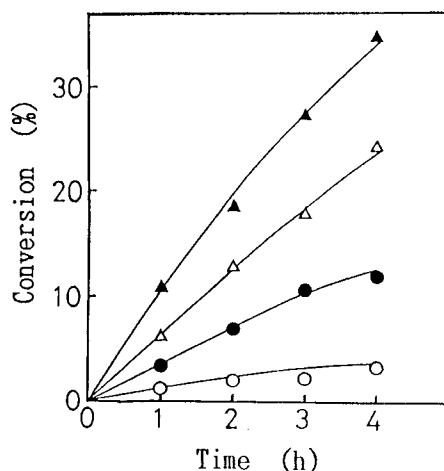
Figure 5.   Time-conversion curves at various total monomer concentration. [ST]=[MAH]=1.67 mol/l. Solvent; Dioxane, [SnCl$_2 \cdot$ 2H$_2$O] = 8.33mmol/l. (O) 30°C, (●) 40°C, (Δ) 50°C, (▲) 60°C.
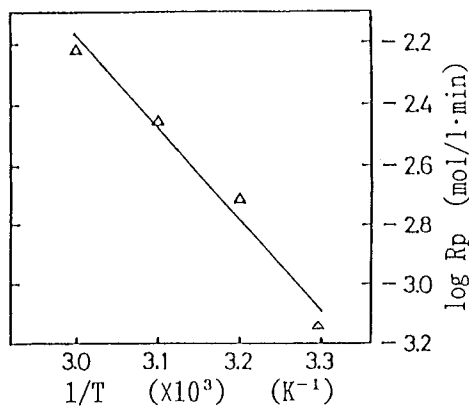

Figure 6.   Arrhenius plots for the copolymerization.

The effect of the temperature on the copolymerization rate of ST with MAH is examined. Figure 5 shows the time-conversion curves of the copolymerization at various temperature initiated by stannous chloride. The initial rate of copolymerization (Rp) increases with increasing polymerization temperature. The overall activation energy as calculated from an Arrhenius plot (Figure 6) was found to be 23.8 Kcal/mol within temperature range 25-60°C.
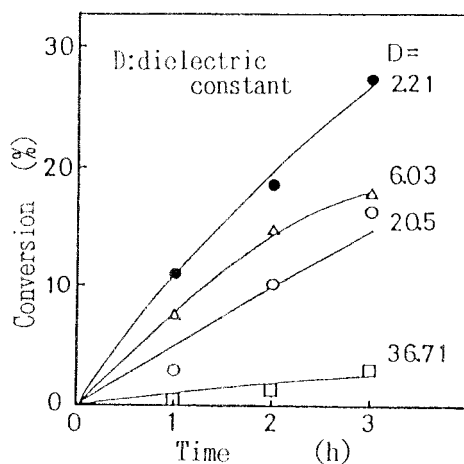
Figure 7. Effect of $SnCl_2 \cdot 2$ H_2O concentration on the rate of the copolymerization. $[ST]=[MAH]=1.67$ mol/l, $[SnCl_2 \cdot 2H_2O] = 8.33$mmol/l, (●) Dioxane, (Δ) Ethyl Acetate, (○) Acetone, □ Dimethyl Formamide.

Figure 7 shows the result of copolymerization of ST with MAH initiated by stannous chloride in the various solvents. Ethyl acetate, acetone and dioxane are good solvents for the copolymerization. Dielectric constant of these solvents are relatively low. These solvents might increase the rate of propagation of primary radicals.

Figure 8 shows the electronic spectra of the systems containing ST,MAH and stannous chloride. As has been reported earlier [11], MAH forms a charge transfer complex with ST in the molar ratio 1:1. As seen from the spectra, it should be noted that the absorbance of the mixture of MAH and stannous chloride is greater than the absorbance of MAH at identical concentration. Neither a new absorption band nor a shifted band of ST appears in the spectrum of the ST-stannous chloride system. After mixing the dioxane solution of stannous chloride with that of MAH, the spectra of the mixed solution of stannous chloride and MAH exhibits an enhanced absorption comparabl with the sum of absorption of the respective components; a point which could be ascribed to charge transfer interaction.

Reaction Mechanism

The observed kinetic results may beexplained by considering a mechanism consisting of the following reactions.
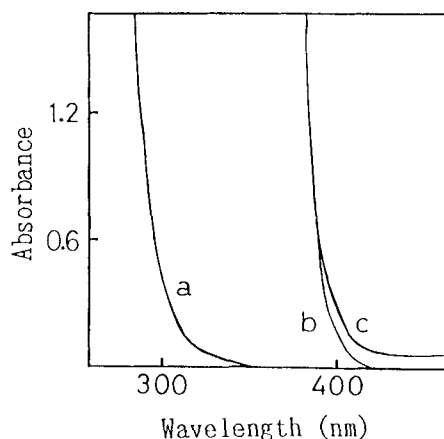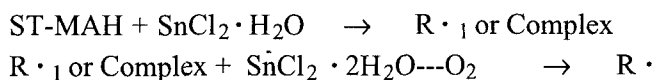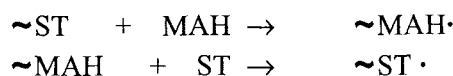
Figure 8. Absorption spectra of charge transfer complex. a) [SnCl$_2$ · 2H$_2$O] =12.5mmol/l; b) [ST]=[MAH]=2.0 mol/l; c) a) + b)

Production of primary radicals R ·, by the interaction of stannous chloride and MAH preceded by the formation of a complex between them. Development of a yellow color in mixing MAH and stannous chloride as well as the extraordinarily high order dependence of the rate of copolymerization might suggest an important participation of a molecular complex formed between MAH and stannous chloride in initiation step of the copolymerization. We proposed the following mechanism.
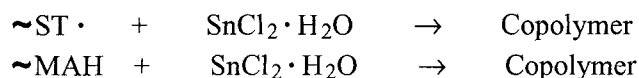
Initiation

$$ST\text{-}MAH + SnCl_2 \cdot H_2O \quad \rightarrow \quad R \cdot {}_1 \text{ or Complex}$$
$$R \cdot {}_1 \text{ or Complex} + SnCl_2 \cdot 2H_2O\text{---}O_2 \quad \rightarrow \quad R \cdot$$

Propagation

$$\sim ST \quad + \quad MAH \rightarrow \quad \sim MAH \cdot$$
$$\sim MAH \quad + \quad ST \rightarrow \quad \sim ST \cdot$$

Termination

$$\sim ST \cdot \quad + \quad SnCl_2 \cdot H_2O \quad \rightarrow \quad \text{Copolymer}$$
$$\sim MAH \quad + \quad SnCl_2 \cdot H_2O \quad \rightarrow \quad \text{Copolymer}$$

The rates of copolymerization were proportional to the first order of the total monomer concentration according to the following usual copolymerization equation under the condition of [M$_1$] = [M$_2$] = [T]/2.

$$\frac{d([M1]+[M2])}{dt} = \frac{(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2)(Ri^{1/2}/\delta_1)}{\{r_1^2[M_1]^2 + 2\phi r_1 r_2[M_1][M_2]\,\delta_2/\delta_1 + r_2^2[M_2]^2(\delta_2/\delta_1)^2\}^{1/2}}$$

with $\delta_1 = 2k_{t11}^{1/2}/k_{p11}$, $\delta_2 = 2k_{t22}^{1/2}/k_{p22}$, $\phi = k_{t12}/2(k_{t11}\cdot k_{t22})^{1/2}$.

Therefore, the rate of copolymerization was proportional to

$$Rp = k[SnCl_2 \cdot H_2O]^{1.0}[ST]^{1.0}[MAH]^{2.0}$$

The proposed mechanism involves the formation of charge transfer complex, in the MAH polymerization initiated by stannous chloride, the starting reaction step between stannous chloride and the MAH forms a charge transfer complex, which breaks down liberating the initiating radicals. Under such conditions MAH radical is active species which initiate the copolymerization. It is believed that the generation of the initiating free radical in these present systems takes place by the abstraction of the loosely bonded hydrogen atoms attached to the MAH group through complex formation with stannous chloride and subsequent decomposition. The initiation of polymerization takes place by the interaction of the initiating free radical with the styrene monomer, leading the formation of more stable macroradical. The propagation follows the successive addition of macroradicals with comonomeric units continuously till the dead polymers are formed by termination.

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