

Polymerization Mechanism of Styrene Catalysed by Ceric Salt containing *n*-Dodecylbenzene Sulphonic Ion and Ethyl Alcohol or Cyclohexanone

KYOJI KAERIYAMA

*Polymerization of styrene in benzene catalysed by a ceric salt containing *n*-dodecylbenzene sulphonic ion and ethyl alcohol or cyclohexanone has been investigated. When ethyl alcohol is applied as a co-catalyst, styrene participates in the initiation reaction and the rate of polymerization is proportional to a monomer concentration to the power 1.8. The termination is the reaction of polymer radical with polymer radical or ceric ion at a low concentration of ceric salt, and the reaction of polymer radical with ceric ion at the higher concentrations. The overall activation energy is 17 kcal/mole.*

When cyclohexanone is applied as a co-catalyst, styrene participates in part of the initiation reaction and the rate of polymerization is proportional to a monomer concentration to the power 1.33. The termination is the combination of polymer radicals. The rate of polymerization is about ten times as high as when ethyl alcohol is applied, and the overall activation energy is 13 kcal/mole. A hypothesis on the mechanism of the initiation and termination is proposed based on the difference between reactivities of free ceric ion and the complex of ceric salt with co-catalyst.

MANY papers have dealt with the polymerization of vinyl monomers initiated by ceric salt since its initiator activity was found¹. The studies have mostly been confined to the polymerization of water-soluble monomers in aqueous systems.

Kaizerman, Plainfield and Mino² obtained oil-soluble ceric salt when ceric ammonium nitrate was reacted with sodium sulphonates. Iwakura *et al.*³ briefly reported the polymerization of styrene catalysed by a ceric salt containing dioctyl sulphosuccinate ion in the presence of various alcohols. The rate of polymerization decreases in the order: 1,2-glycol > primary- > secondary- > tertiary alcohol. Iwakura *et al.*⁴ evaluated the content of hydroxyl end-groups in the resultant polystyrene by a novel spectrophotometric method.

In the polymerization of styrene, carried out by a ceric salt containing *n*-dodecylbenzene sulphonic ion in the presence of various co-catalysts, alcohol, aldehyde and ketone were found to be effective co-catalysts. This paper deals with the polymerization of styrene catalysed by the ceric salt and ethyl alcohol or cyclohexanone.

EXPERIMENTAL

Ceric salt containing *n*-dodecylbenzene sulphonic ion was synthesized². In addition to bands observed in the i.r. spectra of sodium *n*-dodecylbenzene sulphonate, the i.r. spectra of the ceric salt contain bands at 1380 cm⁻¹ due to nitric ion and a shoulder at 3150 cm⁻¹ due to ammonium ion. When the ceric salt was burned in a crucible, 21.14 per cent by weight remained

as ash. Because the i.r. spectra of this ash contain no bands assignable to C—H bonds, ester group, nitric ion, or ammonium ion, this ash was assumed to be ceric dioxide. This suggests that 1.03 of the six nitric ions in the original ceric diammonium hexanitate was substituted by *n*-dodecylbenzene sulphonic ion. The ceric salt is soluble in many organic solvents, but insoluble in alcohols and acetone.

Styrene, ethyl alcohol and cyclohexanone, initially commercially purified materials, were distilled under reduced pressure.

Polymerization was carried out in an ampoule under high vacuum. The polymer was precipitated in methanol, filtered and dried *in vacuo* to a constant weight.

Viscometry was carried out at 30°C in benzene solution. The molecular weight was calculated from the intrinsic viscosity based on the equation⁵

$$\log [\eta] = -4.013 + 0.74 \log M_n$$

Polymer yield was defined as moles of polymer produced per litre.

RESULT

Polymerization catalysed by the ceric salt-ethyl alcohol system

The rate of polymerization should be proportional to the square root of the initiator concentration in the steady state with respect to the radical concentration, if termination is by combination of polymer radicals. However, it should be independent of the initiator concentration if termination is by reaction of polymer radical with initiator. The rate of polymerization would be approximately represented by conversion at a certain time in the initial stages of the reaction.

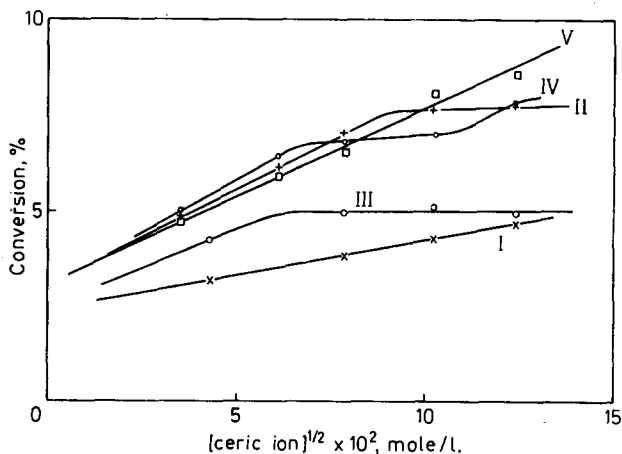


Figure 1—Dependence of conversion on [ceric ion] at 60°C. Curve I: [styrene]=0.873 mole/l.; [EtOH]=1.73 mole/l. time: 72 h. Curve II: [styrene]=2.18 mole/l.; [EtOH]=1.73 mole/l. time: 72 h. Curve III: [styrene]=4.36 mole/l.; [EtOH]=1.73 mole/l. time: 30 h. Curve IV: [styrene]=2.18 mole/l.; [EtOH]=0.873 mole/l. time: 72 h. Curve V: [styrene]=2.18 mole/l.; [EtOH]=2.60 mole/l. time: 72 h

Dependence of conversion on the square root of the ceric salt concentration at different concentrations of styrene and ethyl alcohol are shown in *Figure 1*. Conversion is independent of the initiator concentration at high concentrations and therefore termination is by reaction of polymer radical with ceric ion. Conversion is dependent on the square root of the initiator concentration at lower concentrations, so that the termination contains the combination of polymer radicals. At a concentration of 2.18 mole/l., 0.98 per cent of styrene was thermally polymerized at 60°C after 72 h. Because this value is only about one third of the intercepts in *Figure 1*, the intercepts cannot be interpreted as a result of thermal polymerization of the monomer alone. The termination should contain the reaction of polymer radical with ceric ion even at low concentrations of the initiator.

Termination by ceric ion becomes predominant at lower concentrations of ceric salt as the ethyl alcohol concentration becomes lower.

Dependence of polymer yield on the ceric salt concentration is shown in *Figure 2*. The line corresponds to curve II in *Figure 1*. Polymer yield increases monotonically as the initiator concentration, although conversion is constant at high concentrations of the initiator. This shows that the rate of initiation increases monotonically as the ceric salt concentration, although increase in termination rate cancels increase in initiation rate at high concentrations of the ceric salt.

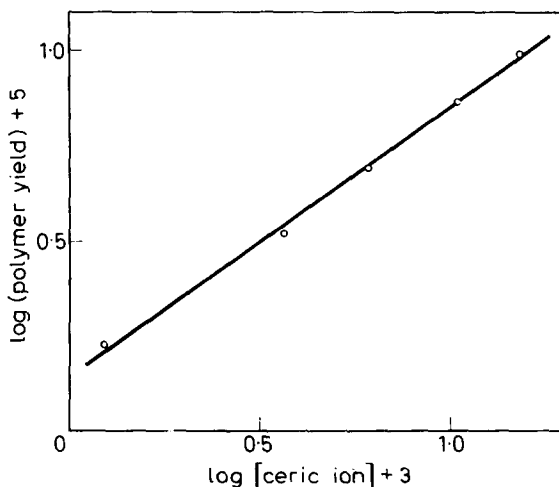


Figure 2—Dependence of polymer yield on [ceric ion] after 72 h at 60°C. [Styrene]=2.18 mole/l.; [EtOH]=1.73 mole/l

Polymer yield should be proportional to the first power of the initiator concentration, because it is proportional to the amount of polymer initiated by the ceric salt. But *Figure 2* shows that it is actually proportional to the initiator concentration to the power 0.71. One of the reasons for this departure might be that the same viscosity/molecular weight relation was applied to all the polymers, which were produced through different termina-

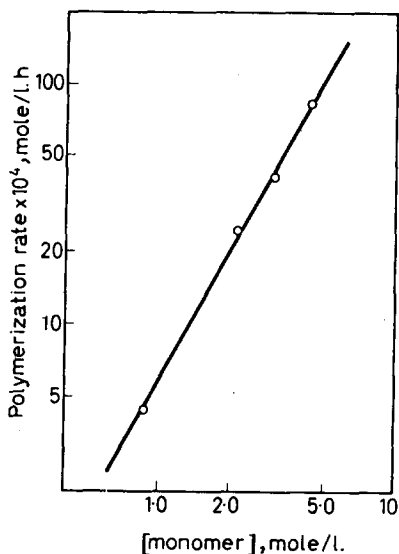


Figure 3—Dependence of polymerization rate on [monomer]. [EtOH]=1.73 mole/l.; [ceric ion]= 6.14×10^{-3} mole/l. Temperature: 60°C

tion mechanisms and therefore have different molecular weight distributions.

The dependence of the initial rate of polymerization on monomer concentration is shown in *Figure 3*. The polymerization rate is proportional to the monomer concentration to the power 1.80. This is considered a significant departure from the first power and suggests that the monomer participates in the initiation reaction.

Dependence of polymer yield on monomer concentration is shown in *Figure 4*. The line shows that polymer yield is expressed thus

$$\text{Polymer yield} = a [M] + b \quad (1)$$

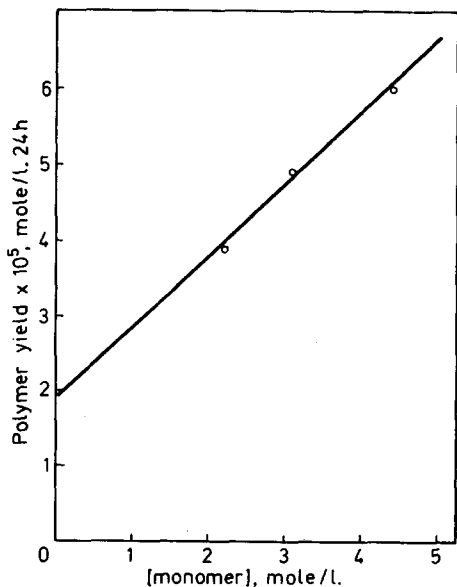


Figure 4—Dependence of polymer yield on [monomer]. [EtOH]=1.73 mole/l.; [ceric ion]= 6.14×10^{-3} mole/l. Temperature: 60°C

where a and b are constants and $[M]$ is monomer concentration. This equation shows that two initiation mechanisms are concerned: one where monomer participates in the initiation reaction and the other where it does not.

Initial rates of polymerization measured over the temperature range 50° to 70°C have been studied. The overall activation energy is 17 kcal/mole .

Polymerization catalysed by the ceric salt-cyclohexanone system

Dependence of conversion on the square root of the ceric salt concentration at different concentrations of styrene and cyclohexanone is shown in Figure 5. Conversion is proportional to the square root of the ceric salt

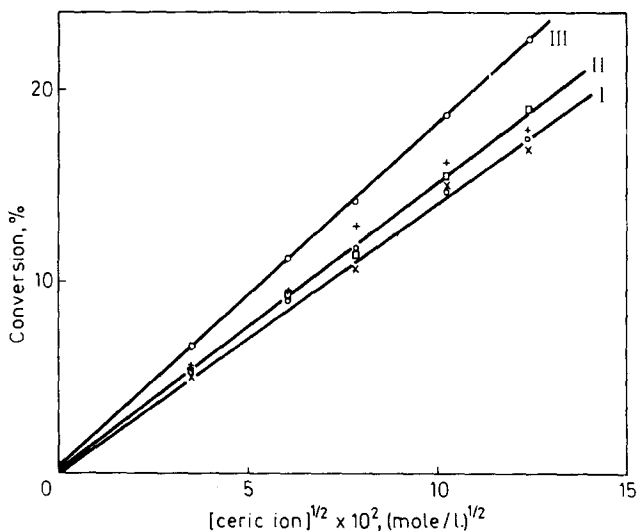


Figure 5—Dependence of conversion on [ceric ion] at 60°C . I: [styrene]= 0.873 mole/l. ; [cyclohexanone]= 0.966 mole/l. ; time, 24 h. II: [styrene]= 2.18 mole/l. ; time, 20 h —O— [cyclohexanone]= 0.338 mole/l. , —+- [cyclohexanone]= 0.966 mole/l. , —□— [cyclohexanone]= 1.93 mole/l. III: [styrene]= 4.36 mole/l. ; [cyclohexanone]= 0.966 mole/l. ; time, 17 h

concentration over the range of styrene and cyclohexanone concentrations studied. This means that termination is by combination of polymer radicals. Conversion is independent of cyclohexanone concentration over the range studied.

Dependence of polymer yield on the ceric salt concentration is shown in Figure 6. The line corresponds to the line II (—+-) in Figure 5. Polymer yield is proportional to the ceric salt concentration to the power 1.07 . This is not considered a significant departure from the first power, because analysis is not made in the initial stage of polymerization and molecular weight is obtained from viscometry.

The dependence of the initial rate of polymerization on monomer con-

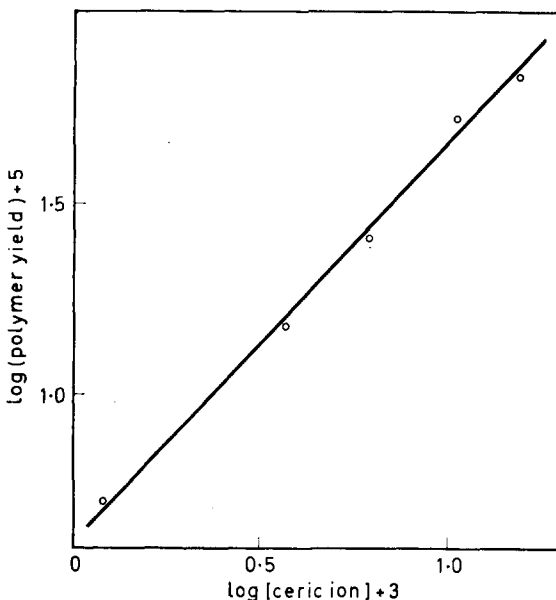


Figure 6—Dependence of polymer yield on [ceric ion] after 20 h at 60°C. [Styrene]=2.18 mole/l.; [cyclohexanone]=0.966 mole/l

centration is shown in *Figure 7*. The polymerization rate is proportional to the monomer concentration to the power 1.33. This is a significant departure from the first power and suggests that monomer participates in part of the initiation reaction.

Dependence of polymer yield on monomer concentration is shown in *Figure 8*. Polymer yield is expressed by an equation of the same type as equation (1), although the gradient is less. This shows that two initiation mechanisms are concerned.

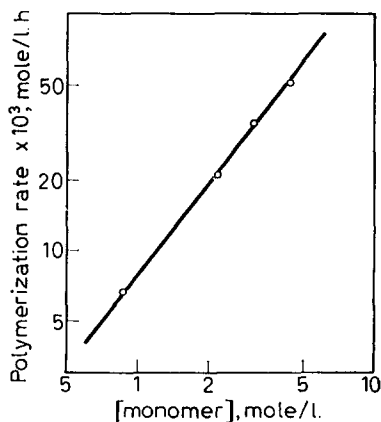


Figure 7—Dependence of polymerization rate on [monomer] at 60°C. [Cyclohexanone]=0.966 mole/l.; [ceric ion]= 6.14×10^{-3} mole/l

POLYMERIZATION MECHANISM OF STYRENE

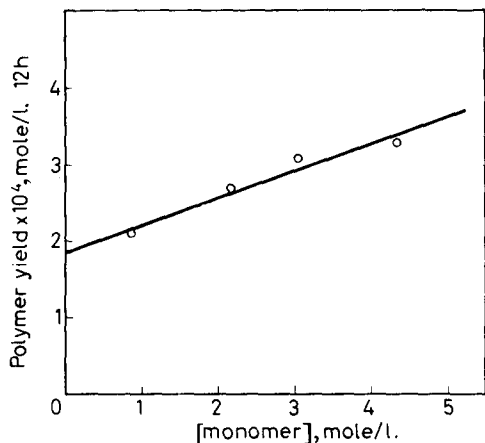


Figure 8—Dependence of polymer yield on [monomer] at 60°C. [Cyclohexanone]=0.966 mole/l.; [ceric ion]= 6.14×10^{-3} mole/l

Results of polymerization in the presence of ethyl alcohol or cyclohexanone are shown in *Table 1*. It is difficult to compare polymers with those that have different molecular weight distributions. However, in this case polymerizations in the presence of ethyl alcohol were carried out under conditions where termination by combination of polymer radicals was predominant, and therefore the resultant polymers probably did not have such different molecular weight distributions as polymers produced in

Table 1. Comparison of co-catalysts

No.	Co-catalyst mol/l.	Ceric salt $\times 10^3$ (mol/l.)	Poly- merization time h	Conversion, %	M_n $\times 10^{-5}$	Polymer yield $\times 10^{-5}$, (mol/l.)
94	EtOH 1.73	1.23	72	4.9	6.6	1.7
95	EtOH 1.73	3.68	72	6.1	4.2	3.3
96	EtOH 1.73	6.14	72	7.1	3.3	4.9
145	cyclohexanone 0.966	1.23	20	5.5	2.4	5.4
146	cyclohexanone 0.966	3.68	20	9.5	1.4	15
147	cyclohexanone 0.966	6.14	20	12.8	1.1	26

Polymerization temperature 60°C

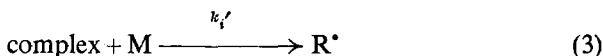
the presence of cyclohexanone. In spite of shorter polymerization times, higher polymer yields were obtained in the presence of cyclohexanone. Polymers produced in the presence of cyclohexanone have lower molecular weight. It is evident that the higher polymerization rates obtained in the presence of cyclohexanone are due to an increased rate of initiation.

Initial rates of polymerization measured over the temperature range 50° to 70°C have been studied. The overall activation energy is 13 kcal/mole.

DISCUSSION

The mechanisms of initiation and termination might be explained reasonably if it was assumed that the complex of ceric salt and co-catalyst

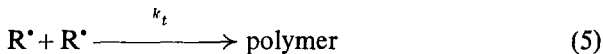
participated in the initiation reaction, but that free ceric ion which is not included in the complex could not participate and might terminate the propagation reaction. Participation of monomer in initiation reaction suggests that the process leading to the generation of free radicals involves a trimolecular mechanism. This may imply the reaction of styrene with the complex of the ceric salt and co-catalyst. Accordingly, the initiation reaction may be written as follows:



where R^* represents the radical. By the free radical R^* produced, the propagation may proceed thus



The termination reaction may then be written:



The initiation rate that corresponds to reactions (2) and (3) is given by

$$R_i = k_i' [\text{complex}] [\text{M}] + k_i [\text{complex}] \quad (7)$$

This equation is of the same type as equation (1). Data described previously show that both terms on the RHS contribute to the initiation rate. The polymerization rate may be given by

$$R_p = k_p [\text{R}^*] [\text{M}] \quad (8)$$

and the termination rate which corresponds to reactions (5) and (6) by

$$R_t = k_t [\text{R}^*]^2 + k_t' [\text{R}^*] [\text{Ce}^{\text{IV}}] \quad (9)$$

The dissociation constant of the complex, K , may be given by

$$K = [\text{Ce}^{\text{IV}}] [\text{co-catalyst}] / [\text{complex}] \quad (10)$$

If K is small, $[\text{Ce}^{\text{IV}}]$ is low, and therefore the steady state with respect to the radical concentration may be represented by

$$k_i [\text{complex}] + k_i' [\text{complex}] [\text{M}] = k_t [\text{R}^*]^2 \quad (11)$$

Substitution of $[\text{R}^*]$ from equation (11) into equation (8) gives

$$R_p = k_p / k_i^{\frac{1}{2}} (k_i + k_i' [\text{M}])^{\frac{1}{2}} [\text{complex}]^{\frac{1}{2}} [\text{M}] \quad (12)$$

This equation represents polymerization in the presence of cyclohexanone. Because K is small and almost all ceric ion is in the form of complex, the polymerization rate is proportional to the square root of added ceric salt concentration. If only the first term in parentheses contributed to the initiation rate, the polymerization rate would be proportional to the first power of monomer concentration: if only the second term contributed to

the initiation rate, it would be proportional to the monomer concentration to the power 1.5. Because both terms actually contribute to the initiation reaction as described above, the polymerization rate is proportional to the monomer concentration to the power 1.33.

If K is large enough, $[Ce^{IV}]$ is high, and therefore the steady state may be represented by

$$k_i [\text{complex}] + k_i' [\text{complex}] [M] = k_t' [R^*] [Ce^{IV}] \quad (13)$$

Substitution of $[R^*]$ from equation (13) into equation (8) gives

$$R_p = k_p / k_t' \cdot K (k_i + k_i' [M]) [\text{co-catalyst}] [M] \quad (14)$$

The polymerization rate is independent of the ceric ion concentration. Because the dissociation constant of the complex with ethyl alcohol is fairly large, the polymerization rate is independent of the ceric salt concentration when the ceric ion concentration is high or the ethyl alcohol concentration is low. However, it depends on the square root of the ceric salt concentration when the ceric salt concentration is low or the ethyl alcohol concentration is high. Because contribution of the term $k_i' [M]$ is important compared with that of k_i , the polymerization rate is proportional to the monomer concentration to the power 1.80.

Table 2. Effect of ceric salt on polymerization initiated by azo-bis-isobutyronitrile

Ceric salt, $\times 10^3$ mol/l.	Polymerization time, h	Yield, mol/l.	Ceric salt $\times 10^3$ mol/l.	Polymerization time, h	Yield, mol/l.
0	1.5	0.043	6.14	3.0	0.004
0	3.0	0.084	6.14	5.0	0.025
0	5.0	0.136	6.14*	3.0	0.066
6.14	1.5	0	6.14†	3.0	0.143

*In the presence of ethyl alcohol (1.73 mol/l.).

†In the presence of cyclohexanone (0.966 mol/l.). $[AIBN] = 3.04 \times 10^{-3}$ mol/l.; $[styrene] = 2.18$ mol/l. The solvent was benzene at a temperature of 60°C.

To see if free ceric ion terminates polymerization or not, the effect of ceric salt on polymerization by azo-bis-isobutyronitrile has been studied. The results are shown in Table 2. Because addition of ceric salt remarkably reduces the yield in the absence of ethyl alcohol or cyclohexanone, it appears that free ceric ion terminates polymerization. Further addition of ethyl alcohol or cyclohexanone recovers the yield. This shows that the complex with co-catalyst does not terminate polymerization.

The Textile Research Institute
of the Japanese Government,
4 Sawatari, Kanagawa-ku,
Yokohama, Japan

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