

질산코발트(II)에 의한 Methyl Methacrylate 의 중합

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Polymerization of Methyl Methacrylate Initiated by Cobalt(II) Nitrate

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요 약. Tetrahydrofuran(THF)중에서 질산코발트(II)를 개시제로 사용하여 methyl methacrylate (MMA)의 중합반응을 연구하였다.

반응속도론적 연구 결과로 다음과 같은 중합속도식을 얻었다.

$$R_p = k [\text{질산코발트(II)}]^{0.5} [\text{MMA}]^{1.5}$$

Chelate를 잘 형성하는 옥살산이 중합속도에 미치는 영향을 고려해 보면, 단위체인 MMA가 질산코발트(II)와 배위착물을 형성한다는 것을 추론할 수 있었다.

또 중합억제물이 존재하면 억제시간이 생기고, 이 중합계의 겐보기 총 활성화 에너지는 14.0 kcal/mole이라는 것을 알았다.

ABSTRACT. The polymerization of methyl methacrylate(MMA) initiated by cobalt(II) nitrate in tetrahydrofuran(THF) has been studied. From the results of kinetic studies, the overall polymerization rate(R_p) could be expressed as following;

$$R_p = k [\text{cobalt(II) nitrate}]^{0.5} [\text{MMA}]^{1.5}$$

By considering the effects of chelating agent on the polymerization rate, it could be assumed that the monomer, MMA might form a coordination complex with cobalt(II) nitrate.

In the presence of radical inhibitor hydroquinone, the inhibition time was observed. And the apparent overall activation energy was calculated to be 14.0 kcal/mole.

1. INTRODUCTION

Metal containing initiator systems which induced free radical vinyl polymerization have been studied extensively. The first of which was redox systems using metal compounds and peroxides as

initiators.

Recently it was reported that metal carbonyls¹, metallic chelates² and Raney metals³ in the presence of suitable organic halides were effective initiators. The initiation mechanism of these systems was explained in the way that the coor-

dination complexes were formed between organic halides and them, and a primary radical was supposed to be produced from these complexes.

It was also reported that metallic salts only such as ceric⁴ cupric⁵ ferric⁶ and silver⁷ salts could induce free radical vinyl polymerization and selectivity for monomer was observed. The coordination mechanism was also introduced in these systems. But in these cases it was appreciated that coordination complexes were formed between monomer and metal salts described above. So the proper choice of monomer was required.

Although it was reported that a few cobalt(III)⁸ and cobalt(II)⁹ complexes could initiate the polymerization of vinyl monomer, there was few reports that cobalt salts could initiate the free radical polymerization of vinyl monomer except for the case of cobalt(II) chloride¹⁰ which was published recently. For the polymerization of methyl methacrylate initiated by cobalt(II) chloride in tetrahydrofuran, the initiation mechanism was explained as following; The coordination complex was formed between cobalt(II) chloride and methyl methacrylate. And the complexed methyl methacrylate (electron acceptor) and non-complexed methyl methacrylate (electron donor) could form the charge transfer complex, from which a diradical was considered to be produced.

So it might be interesting to study the polymerization of methyl methacrylate initiated by cobalt(II) nitrate which was well-known one of the cobalt(II) salts.

2. EXPERIMENTALS

2.1. Materials

Methyl methacrylate(MMA) and tetrahydrofuran(THF) were purified by the same methods as described in the previous paper¹⁰.

Cobalt(II) nitrate($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was re-

crystallized from water and dried in vacuo.

Hydroquinone was recrystallized from methanol and dried in vacuo. Reagent grade, oxalic acid was used without further purification.

2.2 Homopolymerization procedure.

Homopolymerization of MMA was carried out also by the same methods as described in the previous paper¹⁰.

3. RESULTS and DISCUSSIONS

3.1. Kinetic Studies

3.1.1. Effects of Initiator Concentration on the Polymerization Rate. To obtain the relationship between reaction time and conversion for the polymerization of MMA initiated by cobalt(II) nitrate in THF, polymerization was carried out at 40°C where the concentration of MMA in THF was kept constant at 4.70 mole/l and the concentration of cobalt(II) nitrate as a initiator was varied in the range from 1.5×10^{-4} to 2.4×10^{-3} mole/l. The dependence of time-conversion curves on cobalt(II) nitrate concentration was shown in Fig. 1.

As shown in Fig. 1 a linear time-conversion correlation was obtained for the initial stage of

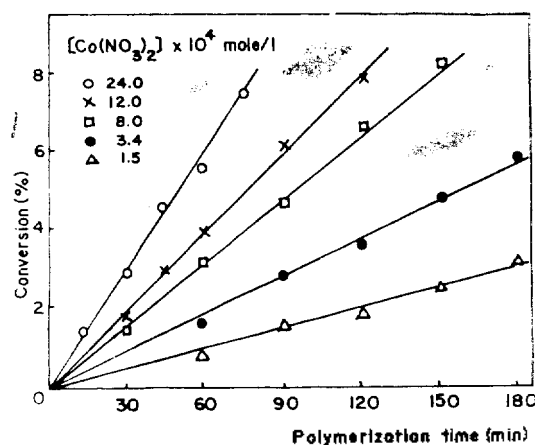


Fig. 1. Time-conversion relations for the polymerization of MMA initiated by various concentrations of $\text{Co}(\text{NO}_3)_2$ in THF at 40°C.

[MMA] = 4.70 mole/l, [THF] = 6.11 mole/l

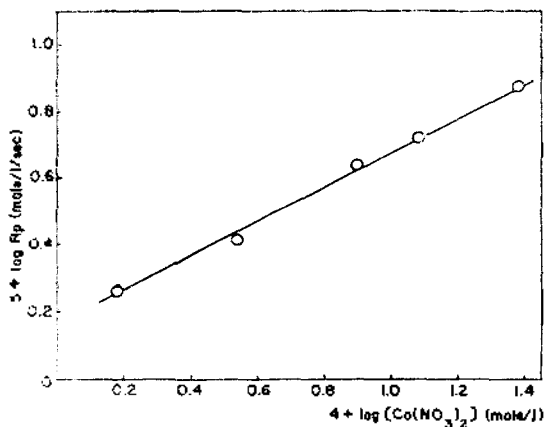


Fig. 2. Relationship between R_p and $[\text{Co}(\text{NO}_3)_2]$ for the polymerization of MMA initiated by $\text{Co}(\text{NO}_3)_2$ in THF at 40°C .

$[\text{MMA}] = 4.70 \text{ mole/l}$, $[\text{THF}] = 6.11 \text{ mole/l}$

polymerization and the polymerization rate was increased with increasing the concentration of cobalt(II) nitrate. Therefore it was possible to calculate the overall polymerization rate (R_p) from the slope of linear time-conversion relations for the initial stage of polymerization.

To estimate the dependence of the polymerization rate on cobalt(II) nitrate concentration, a log-log plot of the polymerization rate vs. cobalt(II) nitrate concentration was given in Fig. 2.

From the slope of straight line in Fig. 2, the reaction order of cobalt(II) nitrate on the polymerization rate was found to be 0.5 which was comparable to 0.37 for cobalt(II) chloride¹⁰. It was well known that the polymerization rate was dependent on 1/2 order of concentration of initiator for a free radical polymerization.

3.1.2. Effects of Monomer Concentration on the Polymerization Rate. Similarly the dependence of polymerization rate on monomer concentration was examined at 40°C where the concentration of cobalt(II) nitrate was kept constant at $12.0 \times 10^{-4} \text{ mole/l}$ and the concentration of MMA was varied in the range from 1.88 to 7.52 mole/l. It was found that the polymerization

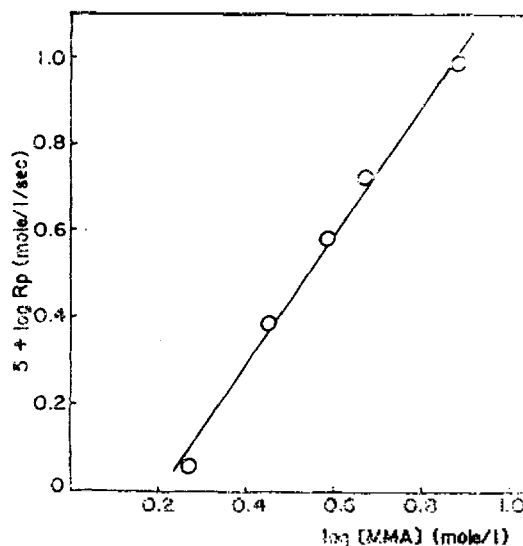


Fig. 3. Relationship between R_p and $[\text{MMA}]$ for the polymerization of MMA initiated by $\text{Co}(\text{NO}_3)_2$ in THF at 40°C .

$[\text{Co}(\text{NO}_3)_2] = 12.0 \times 10^{-4} \text{ mole/l}$.

proceeded linearly with reaction time and the polymerization rate was increased with increasing the concentration of MMA.

From the slope of a straight line for time-conversion curves of the initial stage of polymerization, the polymerization rate was obtained and a log-log plot of the polymerization rate vs. monomer concentration was shown in Fig. 3.

As shown in Fig. 3 a straight line relationship was obtained and the slope of this line indicated that the polymerization rate was dependent on the 1.5 order of concentration of MMA. So the overall polymerization rate (R_p) of this system was given as following equation;

$$R_p = k [\text{Co}(\text{NO}_3)_2]^{0.5} [\text{MMA}]^{1.5} \quad (1)$$

Our experimental reaction order of MMA on polymerization rate was found to be 1.5 and this reaction order could be explained as following; It was known that the polymerization rate was proportional to (cobalt(II) nitrate)^{0.5} as discussed in 3.1.1 and the reaction order of

monomer on polymerization rate was 1.0 for the polymerization of MMA initiated by free radical initiator¹¹. And it has been reported that the 1:1 coordination complex was formed between cobalt(II) nitrate and MMA in dimethylformamide¹². With the above results and the assumption that the polymerization of MMA in this system was initiated by complex formed between cobalt(II) nitrate and MMA as same methods described for cobalt(II) chloride¹⁰, the overall polymerization rate was expressed as following equation which was equivalent to Equation 1;

$$R_p = k [\text{Co}(\text{NO}_3)_2\text{-MMA}]^{0.5} [\text{MMA}]^{1.0} \quad (2)$$

3.1.3. Effects of Temperature on the Polymerization Rate. The dependence of polymerization rate on temperature was examined in the range from 35 to 55 °C where the concentration of MMA and cobalt(II) nitrate in THF were kept constant at 4.70 and 12.0×10^{-4} mole/l respectively, and it was found that the polymerization rate was increased with increasing temperature as shown in Table 1.

The apparent overall activation energy obtained from the Arrhenius plot was found to be 14.0 kcal/mole which was similar to that for cobalt(II) chloride¹⁰.

3.2. Effects of Additives

3.2.1. Effects of Chelating Agent on the Polymerization Rate. In order to confirm that

Table 1. Effects of temperature on polymerization rate for the polymerization of MMA initiated by $\text{Co}(\text{NO}_3)_2$ in THF.

$[\text{MMA}] = 4.70$ mole/l, $[\text{THF}] = 6.11$ mole/l,

$[\text{Co}(\text{NO}_3)_2] = 12 \times 10^{-4}$ mole/l

Temp. (°C)	$R_p \times 10^5$ (mole/l/sec)
35	3.55
40	5.55
45	7.33
50	10.32
55	13.80

MMA participated in the initiation step via complex formation with cobalt(II) nitrate, the polymerization of MMA initiated by cobalt(II) nitrate in THF was carried out at 40 °C in the presence and absence of oxalic acid where the concentration of MMA and cobalt(II) nitrate in THF were kept constant at 4.70 and 12.0×10^{-4} mole/l respectively, and the time-conversion relation was given in Fig. 4.

As shown in Fig. 4 an inhibition period was observed when oxalic acid was present. It was well known that oxalic acid was an effective chelating agent and the formed chelate compound had exceptionally high stability. Therefore in the presence of oxalic acid, cobalt(II) nitrate would easily form the chelate compound with oxalic acid and the resulting relatively stable chelate formation would prevent formation of coordination complex between MMA and cobalt(II) nitrate which was supposed to initiate the polymerization. Thus the polymerization would be inhibited by the presence of oxalic acid. This kind of inhibition was also observed for the cobalt(II) chloride system¹⁰.

3.2.2. Effects of Radical Inhibitor on the Polymerization Rate. The effects of radical

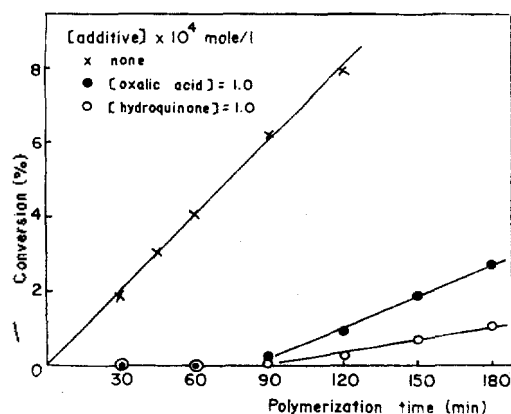


Fig. 4. Effects of additives for the polymerization of MMA initiated by $\text{Co}(\text{NO}_3)_2$ in THF at 40 °C. $[\text{Co}(\text{NO}_3)_2] = 12.0 \times 10^{-4}$ mole/l, $[\text{MMA}] = 4.70$ mole/l, $[\text{THF}] = 6.11$ mole/l.

inhibitor hydroquinone on the polymerization rate was examined at 40 °C under the same condition as above experiment in order to elucidate whether the polymerization of this system proceeded via radical mechanism.

The inhibition time was observed in the presence of hydroquinone as shown in Fig. 4 which was also observed for the polymerization of MMA initiated by cobalt(II) chloride in THF¹⁰.

From the above results it was found that the polymerization of MMA initiated by cobalt(II) nitrate in THF had similar polymerization behavior to that initiated by cobalt(II) chloride.

REFERENCE

1. C.H. Bamford, *et al.*, *Proc. Roy. Soc.*, A 268, 553(1962).
2. T. Otsu, Y. Minami and Y. Nishikawa, *J. Macromol. Sci. Chem.*, A2, 905(1968).
3. T. Otsu and M. Yamaguchi, *J. Polymer Sci.*, B5, 697(1967).
4. H. Narita, Y. Sakamoto and S. Machida, *Makromol. Chem.*, 143, 279(1971).
5. S. Tazuke and S. Okamura, *J. Polymer Sci.*, A-1, 4, 141(1966).
6. H. Narita, Y. Sakamoto and S. Machida, *Makromol. Chem.*, 152, 143(1972).
7. J.P. Hermans and G. Smets, *J. Polymer Sci.*, A3, 3175(1965).
8. Z. Osawa, M. Sorimachi and H. Kanazawa, *J. Polymer Sci.*, A-1, 11, 523(1973).
9. Z. Osawa, T. Shimbamiya and T. Kawamata, *J. Polymer Sci.*, A-1, 8, 2957(1970.)
10. D. Lee and T. Ahn, *J. Korean Chem. Soc.*, 19, 53(1975).
11. C. Walling and L. Heaton, *J. Amer. Chem. Soc.*, 87, 38(1965).
12. F.D. Williams, *J. Macromol. Sci. Chem.*, A2 (3), 459(1968).