NOTES

Polymerization of Methacrylic Esters Initiated by Cyanocobalt(II) Complex in *N,N*-Dimethylformamide

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Cyanocobalt(II) complex prepared at CN:Co < 5:1 is a useful catalyst of cyanation,¹ hydrocyanation,² hydrogenation,³ and polymerization⁴ in aqueous solution. The reactivity and selectivity are influenced remarkably by the molar ratio of CN to Co (CN/Co) in each reaction. We reported hydrogenation³ catalyzed by the complex. The active species has not been elucidated. It was interesting to investigate the catalytic action of the complex as a polymerization initiator to elucidate the active species.

Although the complex has been used in aqueous solution, homogenous solutions of the complex in polar organic solvents were obtained by varying counterion^{5,6} recently. Therefore, we tried to apply the complex to polymerization of vinyl monomers by exchanging potassium cation for bis(triphenylphosphine)nitrogen cation (PNP⁺). It was found that polymerizations of methacrylic esters proceeded selectively only in *N,N*-dimethylformamide (DMF). DMF seems related specifically to the polymerization. It is expected to extensive polymerization or organic synthesis catalyzed by the complex in organic solvent.

EXPERIMENTAL

Materials and Polymerization Procedure and Measurements

All monomers were purified by ordinary

methods. DMF and acetonitrile were of dry solvent (Kokusan). PNP-CN was prepared and purified by the method of Carter *et al.*⁶

Polymerization was carried out in a vessel of 100 cm³ capacity attached two side rooms in dry N₂. After the complex was prepared by mixing CoCl₂ and PNP-CN solutions for one minute, it was mixed with 5 cm³ of monomer; total volume of the solution being kept constant at 20 cm³. The vessel was shaken constantly and kept at 35 ± 0.1°C shielded from light. 0.02 cm³ of the reaction solution was drawn out with a microsyringe and diluted with 3 cm³ of tetrahydrofuran (THF) to measure the molecular weight distribution and average of molecular weight (*M_w*) with a TOSOH HLC-8020 and LS-8000 using TSKgel G(2,3,4,5 × 10³)PXL at 40°C in THF.

The reaction solution was poured into a large excess of methanol to precipitate polymer. The conversion was calculated from the weight of the dried polymer.

RESULTS AND DISCUSSION

Selectivity of Solvent and Monomer

Cyanocobalt(II) complex prepared at PNP-CN/CoCl₂ < 5 was dissolved homogeneously in DMF, DMSO, acetonitrile, and acetone. In these solvents, polymerizations of vinyl monomers in Table I were carried out at CN/Co = 1~6 respectively in N₂. It was found that polymerizations of monomers in

Table I. Polymerization of vinyl monomers^a

Monomer	Conversion/%	Time/h
Methyl methacrylate	78.9	30
Ethyl methacrylate	69.5	30
<i>n</i> -Butyl methacrylate	62.0	30
Benzyl methacrylate	88.2	30
Methyl acrylate	2.3	97
Styrene	1.6	70

^a CN/Co, 2; [Co], $1.25 \times 10^{-3} \text{ mol dm}^{-3}$; monomer, 5 cm^3 ; 20 cm^3 of DMF solution in N_2 at 35°C .

Figure 1. Effects of the CN/Co ratio on the polymerization of MMA: Inserted numerals are CN/Co; [Co], $1.25 \times 10^{-3} \text{ mol dm}^{-3}$; MMA, 5 cm^3 ; 20 cm^3 of DMF solution in N_2 at 35°C .

Table I proceeded only in DMF and were fastest at CN/Co=2. The values of polymerization conversion at CN/Co=2 in DMF are listed in Table I. Polymerization activity on methacrylic esters was high selectively.

As shown in Figure 1, the polymerization of MMA proceeded fastest at CN/Co=2 while quite slowly at CN/Co $\geq$ 5 owing to long induction period. The effects of the conversion on M_w of poly(MMA) at CN/Co=2 is shown in Table II. M_w of poly(MMA) increased with polymerization.

Active Species

IR and VIS spectra of cyanocobalt(II) complex in DMF and acetonitrile have been

Table II. Effects of the conversion on the M_w of poly(MMA)^a

Conversion/%	M_w	M_w/M_n
26.7	4.63×10^4	1.5
41.6	5.96×10^4	1.8
69.1	8.40×10^4	1.9
78.9	1.07×10^5	2.0

^a CN/Co, 2; [Co], $1.25 \times 10^{-3} \text{ mol dm}^{-3}$; MMA, 5 cm^3 .

investigated by Carter *et al.*⁶ They suggest the presence of $[\text{Co}(\text{CN})_4]^{2-}$, $[\text{Co}(\text{CN})_3(\text{solvent})]^-$, $[\text{Co}(\text{CN})_2(\text{solvent})_2]$, and $[\text{Co}(\text{CN})\text{Cl}(\text{solvent})_2]$ in the complex solution at CN/Co < 5. Equilibrium is maintained among these complexes. As shown in Figure 1, the active species of the polymerization seems present most at CN/Co=2 and absent at CN/Co $\geq$ 5 at an early reaction time, which is responsible for the induction period of polymerization at CN/Co $\geq$ 5. Based on the selectivity of solvent and monomer, it is assumed that the active species of polymerization is a Co(II) complex intermediate related to CN, DMF and monomer; methacrylic esters are easy to form the intermediate.

Further investigation is required for the elucidation of the active species.

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