

Polymerization of Polar Vinyl Monomers with Novel Cobalt-based Catalyst

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Cobalt-based complex $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3\text{Co}(\text{BH}_4)$ (1) polymerized polar vinyl monomers like acrylonitrile (AN) and methyl methacrylate (MMA) without any cocatalysts. The molecular weight of the poly(AN) was fairly high at around 500×10^3 . It was concluded that the polymerizations did not proceed with radical polymerization mechanism based on the copolymerization results with styrene. The obtained poly(AN) had an atactic structure.

The polymerization of olefins by transition metal catalysts has been intensively studied, and achieved highly stereospecific polymerization using bridged metallocene complexes.¹⁻³ On the other hand, the polymerizations of polar vinyl monomers are generally more difficult because their polar side group often coordinates to the active metal site to prevent the polymerization. Only few examples of precision coordination polymerization of polar vinyl monomer, which include stereospecific⁴ and living⁵ polymerization of MMA, have been reported thus far. And in AN polymerization, although several late transition metal⁶ and rare earth metal⁷ catalysts have been known, the catalytic performance are relatively behind in terms of the precise control of polymer structures. Complex carrying bridged ligand has hardly been examined for the polymerization of AN. In the present paper, the polymerization of polar vinyl monomers like AN by novel cobalt-based catalyst 1,⁸ which has a bridged tripod phosphorus ligand, will be reported.

Table 1 summarizes polymerization of various vinyl monomers with 1. The polymerization was carried out under dry nitrogen atmosphere.⁹ Polar vinyl monomers having electron-withdrawing group were polymerized by 1 without using any cocatalyst. Among the monomers examined, the polymerization activity of AN was the highest to produce white poly(AN) in good yield. This was clearly different from the polymerization by the previously reported cobalt hydride complex³ which showed the higher activity against

methacrylonitrile than AN. It could be checked that the polymerization of AN by 1 was completed within tens of minutes. The molecular weight of the poly(AN) reached 520×10^3 .¹⁰ Methacrylonitrile, methyl acrylate, MMA also produced polymer by 1, though polymer yield and molecular weight remained lower. No polymer was obtained from olefins such as ethylene and propylene, and from vinyl monomers without electron-withdrawing group.

Table 2 details the solvent effect on the polymerization of AN by 1. The polymerization proceeded most effectively in DMF which is a good solvent of both poly(AN) and the catalyst. In another solvents, poly(AN) precipitated during the polymerization. Polymer yield and molecular weight greatly depended on the polarity of the solvent, and decreased with decreasing polarity of the solvent. In hexane the polymerization hardly occurred. Thus, both the solubility of polymer and the polarity of the solvent may influence the activity. In DMF, the polymer yield and molecular weight decreased with a decrease in the polymerization temperature, though poly(AN) formed even at -30°C .

Table 2. Polymerization of AN by 1^a

Solvent	Temp/°C	Yield/%	$M_n/10^3$	Polymer structure/%		
				mm	mr	rr
DMF	20	51	520	29	48	23
DMF	0	26	75	27	50	23
DMF	-30	12	34	27	49	24
CH_2Cl_2	20	22	21	30	48	22
Toluene	20	8	9	31	49	20
Hexane	20	trace				

^a Polymerized for 24 h, [AN] = 7.5 mol dm⁻³, [1] = 7.5 mmol dm⁻³.

To make clear the polymerization mechanism, copolymerization of AN with styrene (St) was attempted. The ¹H NMR spectrum of the product obtained by the copolymerization of equimolar amount of AN and St by 1 was measured in DMF-d₆. No peaks assignable to St unit were observed, indicating that only AN homopolymer was produced (Figure 1(a)). Aromatic peaks did not appear even when [St]/[AN] increased, though the polymerization activity greatly decreased. In radical copolymerization by 2,2'-azobisisobutyronitrile (AIBN) under the equivalent condition, random copoly(AN-St) was formed, and peaks of both AN and St unit were observed in ¹H NMR spectrum as shown in Figure 1(b). Since reactivity ratio of radical copolymerization is hardly affected by the polymerization conditions, it can be said that the polymerization of AN by 1 does not proceed with radical polymerization mechanism.

Table 1. Polymerization by 1^a

Monomer	Polymer yield/%	$M_n/10^3$
Acrylonitrile	51	520
Methacrylonitrile	16	32
Methyl acrylate	5	18
Methyl methacrylate	23	43
Ethylene	0	-
Propylene	0	-
Styrene	0	-
Isobutylvinylether	0	-

^a Polymerized in DMF at 20 °C for 24 h, [Monomer] = 7.5 mol dm⁻³, [1] = 7.5 mmol dm⁻³.

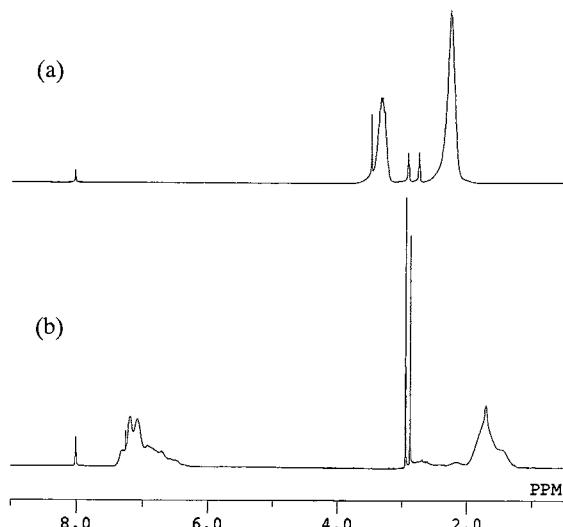


Figure 1. ^1H NMR spectra (a) AN-St by 1 (b) AN-St by AIBN.

Main chain structure of the polymers obtained with 1 was checked. Figure 2 shows the methine carbon region of ^{13}C NMR spectrum of the poly(AN)¹¹ measured in DMF-d_6 . The peaks are assigned to isotactic, heterotactic, and syndiotactic triads from high field to low field, respectively. The intensity ratio of these three peaks were similar to the poly(AN) having an atactic structure. Figure 3 illustrates ^1H NMR spectrum of the poly(MMA)¹¹ measured in CDCl_3 . According to the α -methyl proton around 1.0 ppm, the poly(MMA) possessed syndiotactic-rich atactic structure. The polymerization conditions did not affect the polymer structure in both monomers. Thus, no stereospecific polymerization was attained by 1. This is probably because the ligand of 1 has a symmetric structure.

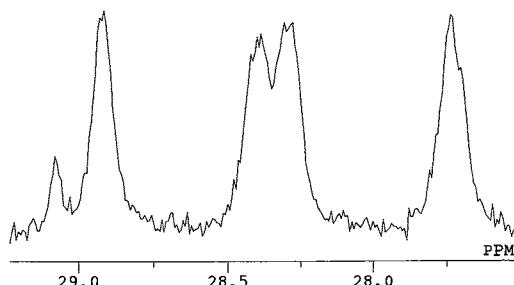


Figure 2. ^{13}C NMR spectrum of poly(AN).

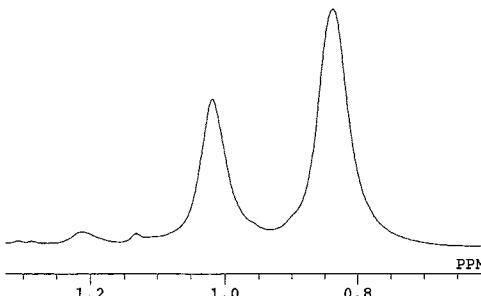


Figure 3. ^1H NMR spectrum of poly(MMA).

In conclusion, polar vinyl monomers were polymerized by 1 without using any cocatalysts. The further study aiming at the control of the polymer structure is now in progress.

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References and Notes

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- 8 1 was synthesized according to the literature: P. Dapporto, S. Midollini, A. Orlandini, and L. Sacconi, *Inorganic Chemistry*, **15**, 2768 (1976).
- 9 Polymerization procedure was as follows: In a 20 mL schlenk tube 1 was dissolved in dry DMF followed by aging for 10 min at room temperature. Solution of monomer was then added by syringe. For ethylene and propylene polymerization, 100 mL stainless steel reactor was used. After polymerization, the solution was poured into dilute HCl solution of methanol to remove the catalyst, filtered, and dried in vacuo. Polymer yield was determined by weighing methanol insoluble product.
- 10 Polymer molecular weight was determined by size exclusion chromatography measured in DMF at 40 °C.
- 11 The polymers were synthesized at 20 °C for 24 h in DMF, [monomer] = 7.5 mol dm⁻³, [1] = 7.5 mmol dm⁻³.