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Novel polymerization of divinyl monomer to polyester catalyzed with organocobaloxime

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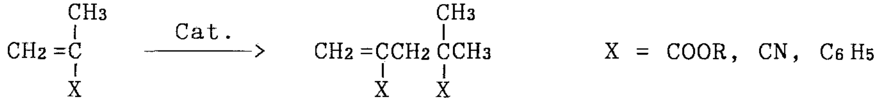
Abstract

The polymerization of ethylene bis(α-ethylacrylate) to polyester was catalyzed with benzyl(bisdimethylglyoximato)(pyridine)cobalt(III). Although the α-ethylacrylic ester does not radically homopolymerize, radical addition to the carbon-carbon double bond yields the corresponding radical. This radical readily reacts with the cobalt(II) complex involved to form a carbon-cobalt bond. Dissociation of the generated bond accompanying fast β-hydrogen elimination results in a new carbon-carbon double bond and the cobalt hydride which rapidly adds to the ethylacrylate moiety to form a carbon radical which may react with the cobalt(II) complex. Through the sequence of these reactions, the novel polyester linkage was expected to be formed. Actually, the cobaloxime catalyzed reaction competed with radical propagation, and the polymer consisted of the polyester linkage (32%) and the consecutive ethylacrylate units with two types of unsaturated pendant groups (68%).

Introduction

Some cobalt complexes such as tetraarylporphyrin and dimethylglyoxime compounds have been used as catalytic chain transfer agents for the radical polymerization of methacrylic monomers, effectively reducing the molecular weight of the polymer.[1-5] The main disadvantage of the catalytic chain transfer is uncontrollable reduction of the molecular weight to the range of oligomer. The catalysts have also been employed to synthesize dimers from α-methylvinyl monomers,[6,7] and some of the dimers can be addition-fragmentation chain transfer agents.[7]



$$CH_2{=}\overset{CH_3}{\underset{X}{C}} \xrightarrow{Cat.} CH_2{=}\underset{X}{C}CH_2\overset{CH_3}{\underset{X}{C}}CH_3 \qquad X = COOR,\ CN,\ C_6H_5$$

The same reaction has been known in organic synthesis as one of the carbon-carbon bond forming reactions via a radical mechanism.[8] Therefore, an appropriate divinyl compound, in which ester bonds connect the vinyl groups, could yield a polymer with a main chain involving heteroatoms through the cobalt complex catalyzed reactions. Such a process could be a novel route to a polymer consisting of a hydrolyzable polyester linkage. Taking into account the dimer formation and lack of polymerizability, we chose ethylene bis(α-ethylacrylate) (EBEA) as the monomer and benzyl(bisdimethylglyoximato)(pyridine)cobalt(III)

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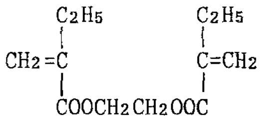
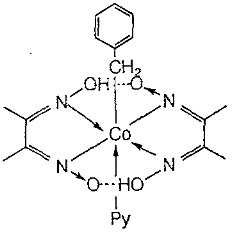
(BBPCo(III)) as the catalyst to prepare the novel polymer.

So far, the polyamide[9] and polyester[10,11] have been prepared from acrylamide and acrylic acid by hydrogen-transfer reactions, respectively. Both polymerizations involve nucleophilic addition to the carbon-carbon double bonds. Limited types of polymers with backbones involving heteroatoms have been prepared by radical mechanism such as ring opening polymerization[12] and copolymerizations of sulfur dioxide, carbon monoxide or oxygen with vinyl monomers.[13]



$$\begin{array}{ccc} C_2H_5 & & C_2H_5 \\ CH_2=\overset{|}{C} & & \overset{|}{C}=CH_2 \\ \overset{|}{} & & \overset{|}{} \\ \multicolumn{3}{c}{COOCH_2CH_2OOC} \end{array}$$

EBEA



BBPCo(III)

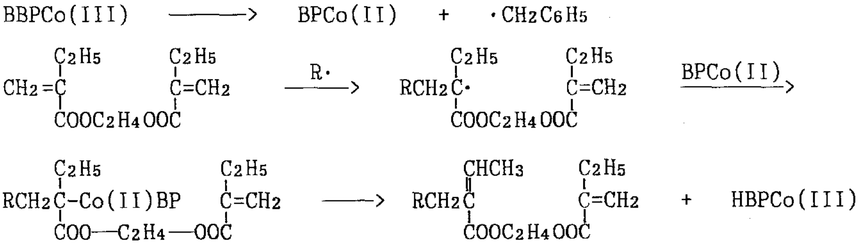
Experimental

EBEA was prepared by the acid catalyzed esterification of α-ethylacrylic acid with ethylene glycol. ^{1}H-NMR ($CDCl_3$): δ = 1.08 (t, 3H, CH_3), 2.30 (q, 4H, CH_2), 4.41 (s, 4H, OCH_2), 5.56 (s, 1H, CH=C), and 6.16 (s, 1H, CH=C). ^{13}C-NMR ($CDCl_3$): δ = 12.60 (α-CH_3), 24.74 (α-CH_2), 62.19 (OCH_2), 124.06 (CH_2=), 141.87 (=C), and 166.90 (C=O). BBPCo(III) was prepared as described in the literature.[14] Commercial 2,2'-azobisisobutyronitrile (AIBN) was recrystallized from methanol. Polymerizations were run in sealed tubes containing EBEA, BBPCo(III), and AIBN. After the polymerization, the contents of the tube were poured into a large amount of n-hexane to isolate the products. Hydrolysis of the polymer was performed in a 30% methanol solution of potassium hydroxide for 30 h at refluxing temperature. The resultant reaction mixture was neutralized by hydrochloric acid and potassium chloride precipitated was removed by filtration. The methanol was evaporated to obtain the hydrolysis products as colorless powder.

Number and weight average molecular weights ($\overline{M}_n$ and $\overline{M}_w$), and polydispersity ($\overline{M}_w/\overline{M}_n$) with reference to standard polystyrenes were measured using a TOSO 8000 series HPLC equipped with columns for gel permeation chromatography and tetrahydrofuran was used as the eluent. ^{1}H- and ^{13}C-NMR spectra were taken by a JEOL α-400 spectrometer using deuteriochloroform as the solvent.

Results and Discussion

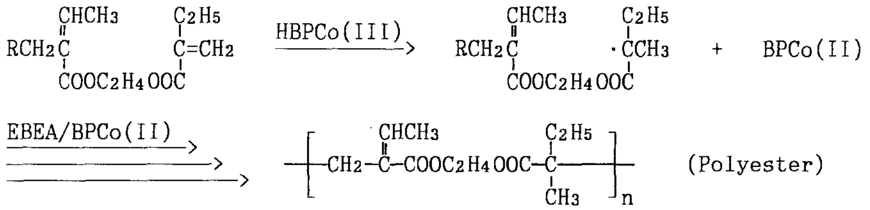
If the carbon-carbon bond formation occurred as expected, the polymerization could proceed via the following reactions:



$$BBPCo(III) \longrightarrow BPCo(II) + \cdot CH_2C_6H_5$$

$$\begin{array}{lll} & C_2H_5 & C_2H_5 \\ CH_2= & \overset{|}{C} & \overset{|}{C}=CH_2 \\ & \multicolumn{2}{l}{\overset{|}{C}OOC_2H_4OO\overset{|}{C}} \end{array} \xrightarrow{R\cdot} \begin{array}{lll} & C_2H_5 & C_2H_5 \\ RCH_2 & \overset{|}{C}\cdot & \overset{|}{C}=CH_2 \\ & \multicolumn{2}{l}{\overset{|}{C}OOC_2H_4OO\overset{|}{C}} \end{array} \xrightarrow{BPCo(II)}$$

$$\begin{array}{lll} & C_2H_5 & C_2H_5 \\ RCH_2 & \overset{|}{C}\text{-}Co(II)BP & \overset{|}{C}=CH_2 \\ & \multicolumn{2}{l}{\overset{|}{C}OO\text{—}C_2H_4\text{—}OO\overset{|}{C}} \end{array} \longrightarrow \begin{array}{lll} & CHCH_3 & C_2H_5 \\ RCH_2 & \overset{\|}{C} & \overset{|}{C}=CH_2 \\ & \multicolumn{2}{l}{\overset{|}{C}OOC_2H_4OO\overset{|}{C}} \end{array} + HBPCo(III)$$



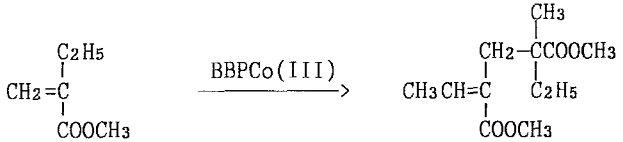
$$\mathrm{RCH_2C(=CHCH_3)COOC_2H_4OOC(C_2H_5)C{=}CH_2} \xrightarrow{\mathrm{HBPCo(III)}} \mathrm{RCH_2C(=CHCH_3)COOC_2H_4OOC(C_2H_5)\cdot CCH_3} + \mathrm{BPCo(II)}$$

$$\xrightarrow{\mathrm{EBEA/BPCo(II)}} \left[\mathrm{CH_2{-}C(=CHCH_3){-}COOC_2H_4OOC{-}C(C_2H_5)(CH_3)}\right]_n \quad \text{(Polyester)}$$

R· may be a benzyl radical from BBPCo(III),[15] the 2-cyano-2-propyl radical from AIBN, or the radical from EBEA. BP denotes the (bisdimethylglyoximato)(pyridine) ligands of the cobalt complexes, and HBPCo(III) is a transient cobalt hydride that adds to the α-ethylacrylate moiety. The polyester linkage may be produced by addition of this radical to EBEA followed by the reaction with BPCo(II) and the subsequent cleavage of the carbon-Co(III) bond accompanied by the β-hydrogen elimination.

If the sequence of these reactions catalyzed with the cobalt complex is much faster than the radical propagation, the polymer should consist of only the polyester linkage. Because the cobalt complex catalyzed polymerization seems to be competitive with the radical propagation, the main chain of the polymer is considered to involve the consecutive ethylacrylate moieties and the polyester linkage.

An internal carbon-carbon double bond may be produced by cleavage of the carbon-Co(III) bond, because dimerization of methyl α-ethylacrylate in the presence of a large amount of BBPCo(III) yielded 5-methyl-3,5-dicarbomethoxy-2-heptene:[7]



$$\mathrm{CH_2{=}C(C_2H_5)COOCH_3} \xrightarrow{\mathrm{BBPCo(III)}} \mathrm{CH_3CH{=}C(COOCH_3){-}CH_2{-}C(CH_3)(C_2H_5)COOCH_3}$$

Faster carbon-carbon bond formation could be predicted for ethylene bismethacrylate from the faster dimer and oligomer formation of methyl methacrylate than that of methyl α-ethylacrylate.[7] However, the radically polymerizable nature of the methacrylate moiety resulted in a crosslinked insoluble product.

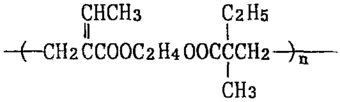
Heating EBEA involving a small amount of AIBN in the presence of BBPCo(III) for 36 h at 60°C, we isolated polymeric products as colorless materials. **Table** 1 summarizes the results of the bulk polymerization at a constant [AIBN]. At the highest [BBPCo(III)] in this table, the resultant polymer consisted of about one-third of the polyester linkage arising from the desired reactions. A decrease in [BBPCo(III)] brought about an increase in polymer yield and a decrease in the content of the polyester linkage. A decrease in [BBPCo(III)] also resulted in increases in $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$. These findings can be expected by the slow cobalt complex catalyzed polymerization relative to the radical addition to the pendant double bond. When [BBPCo(III)] was further decreased, the polymer with a higher $\overline{M}_n$ and a greater $\overline{M}_w/\overline{M}_n$ might be obtained. At the lowest [BBPCo(III)] in **Table** 1, chain extension by the radical propagation including the addition to the pendant double bond was interrupted by the cobalt catalyzed reaction to the lowest extent. However, the lack of polymerizability of the ethylacrylate resulted in a low yield of the polymer.

Table 1. Bulk polymerization of EBEA in the presence of BBPCo(III) for 36 h at 60°C[a)]

[BBPCo(III)] / [EBEA]x10^{-4}	[AIBN] / [BBPCo(III)]	Yield (%)	Polyester linkage[b)] (%)	$\overline{M}_n$	$\overline{M}_w$ / $\overline{M}_n$
5.1[c)]	5.4	13	32	5100	1.2
2.5	11	23	9	3000	5.7
2.0	14	29	5	9300	9.6
1.5	18	4.2[d)]	–	–	–

a) [EBEA] = 4.4 mol/L and [AIBN] = 0.012 mol/L.

b) Content of

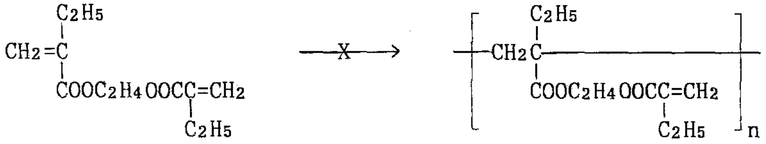


$$-\!\left(\!-CH_2\overset{\overset{CHCH_3}{\|}}{C}COOC_2H_4OOC\overset{\overset{C_2H_5}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_2-\!\right)_{\!n}\!-$$

c) The upper limit of the solubility of the catalyst in the polymerization mixture.

d) Insoluble polymer.

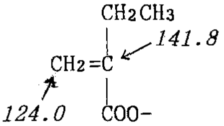
Addition of the radical from the α-ethylacrylate moiety to EBEA could form consecutive units from the ethylacrylic moieties incorporated in main chain. Slow polymerization and a relatively low ceiling temperature do not allow soluble polymer formation of the α-ethylacrylate by AIBN initiated polymerization in the absence of the cobalt catalyst.[16]

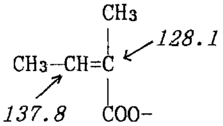


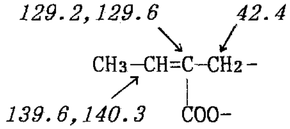
The spectrum of the polymer shown in **Fig.** 1 is more complicated than that expected for the pure polyester. Referring to the resonances of EBEA and its dimer,[7] we can assign the resonances. The two sets of the resonances at 5.55–6.95 ppm are attributed to the *cis*- and *trans*-protons of the methylene and methine with respect to the carbonyl groups (*i* and *j*). The resonances at 4.0–4.5 ppm are due to the methylene protons (*h*) of the ester alkyl groups. A multiplet at 2.4–2.8 ppm can be assigned to the methylene protons (*g*) of the main chain. The resonances at 0.6–2.4 ppm are due to the protons of the methyl groups (*a, b, d,* and *e*) and those of the methylene groups (*c* and *f*).

The alkaline hydrolysis of the polymer took place readily accompanying an apparent decrease in molecular weight as predicted from a low viscoisty of the resultant reation mixture. Detection of α-ethylacrylic acid indicates the presence of the pendant ethylacryloyloxy group.

The main structure of the repeating units was also confirmed from the ^{13}C-NMR spectrum of the same polymer, and the chemical shifts of the characteristic carbons in ppm are as follows:







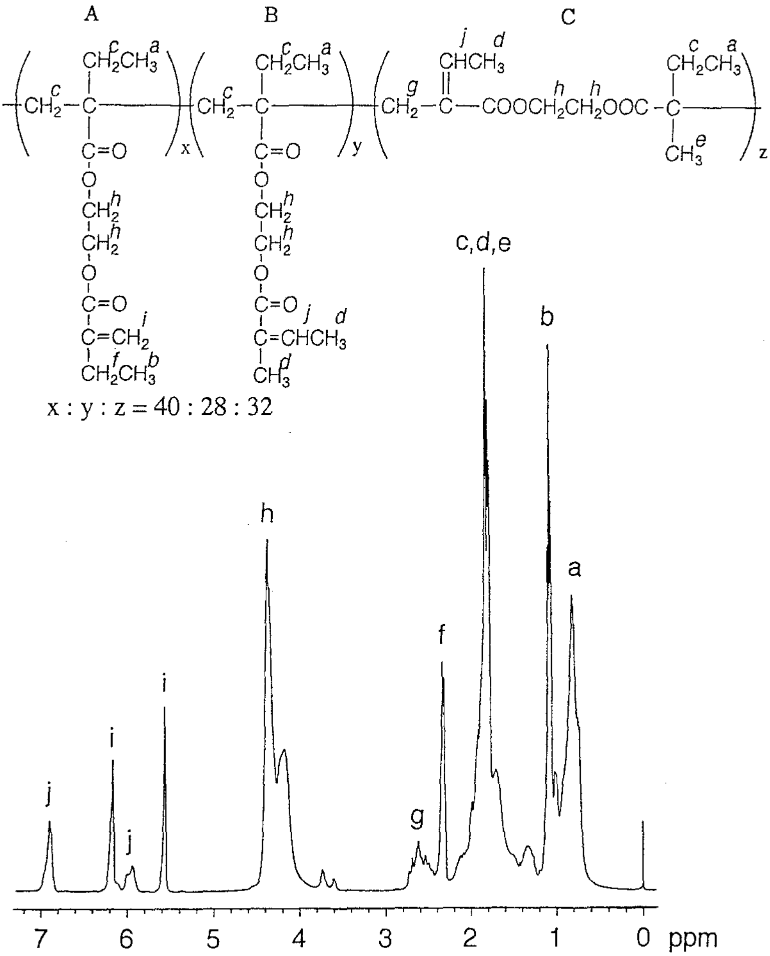


Fig. 1. ^{1}H-NMR spectrum of the polymer ($\bar{M}_n$ = 51000 and $\bar{M}_w/\bar{M}_n$ = 1.2) prepared in bulk catalyzed with BBPCo(III) for 36 h at 60°C: [EBEA] = 4.4 mol/L, [AIBN] = 0.012 mol/L, and [BBPCo(III)] = 2.2×10^{-3} mol/L

Therefore, the polymer yielding the spectrum in **Fig. 1** is confirmed to consist of three types of repeating units, A, B, and C. The contents of these units were calculated from the intensity ratios of the resonances of *g*, *i*, and *j*. The methylene group assigned to *g* is characteristic of the C unit, and the *j* protons are involved in the B and C units. Only the A unit contains the methylene group exhibiting the resonance of *i*. The composition of the polymer of which the ^{1}H-NMR spectrum is shown in **Fig. 1** was calculated from the intensity ratios of the characteristic resonances: x : y : z = 40 : 28 : 32.

Table 2 summarizes the results of the bulk polymerization at a constant [BBPCo(III)]. An increase in [AIBN] brought about an increase in polymer yield and a decrease in the content of the C unit. At the lowest [AIBN] in this table, about one-third of the polymerization steps occurred through the cobalt complex catalyzed reaction. The yield and the content of the C unit decreased and increased, respectively, with an increase in [AIBN]. Although an increase in [AIBN] reduced the content of the C unit, the polymer with a higher $\overline{M}_n$ was isolated. This tendency is ascribable to an increase in the contribution of the radical propagation leading to the A or B unit. When [AIBN] was increased further, the polymer with a greater $\overline{M}_w/\overline{M}_n$ and a lower content of the C unit arising from the faster addition to the pendant double bond was obtained. At a higher [AIBN], the addition to the pendant double bond could further increased $\overline{M}_w/\overline{M}_n$ at a slightly higher $\overline{M}_n$.

According to the results in **Tables** 1 and 2, a low [AIBN] and a high [BBPCo(III)] are preferable for the polyester formation. Concurrence of the radical propagation seems to be required, because the polyester formation from EBEA is not sufficiently fast even under the optimum conditions. Combination of the polyester formation and the radical propagation could afford the novel polymer from the bisethylacrylate and similar compounds such as *p,p'*-diisopropenylbiphenyl.

Table 2. Bulk polymerization of EBEA in the presence of BBPCo(III) for 36 h at 60°C[a)]

$\frac{[\mathrm{AIBN}]\times 10^3}{[\mathrm{EBEA}]}$	$\frac{[\mathrm{AIBN}]}{[\mathrm{BBPCo(III)}]}$	Yield (%)	Polyester linkage[b)] (%)	$\overline{M}_n$	$\frac{\overline{M}_w}{\overline{M}_n}$
0.69	2.7	2	32	2800	1.8
1.4	5.4	3	16	3500	1.8
2.8	11	23	9	3000	5.7
3.2	13	30	9	3100	8.5

a) [EBEA] = 4.4 mol/L and [BBPCo(III)] = 1.1 x 10^{-3} mol/L.
b) See **Table** 1.

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