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STEREOREGULAR POLYMERIZATION OF ALKYL PROPIOLATE CATALYZED BY Rh COMPLEX

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ABSTRACT

The polymerizations of alkyl esters of propiolic acid by Rh complex catalysts were investigated. [Rh(norbornadiene)Cl]$_2$, which was the most active among the catalysts examined, gave rise to poly(alkyl propiolate) in a fairly high yield (~80%) in the presence of alcohol as the polymerization solvent. The polymers formed were a pale yellow powder soluble in common organic solvents except for poly(methyl propiolate). The structures of the polymers obtained were investigated by IR, ^{13}C-NMR, CP MAS ^{13}C-NMR, and laser Raman spectroscopies, together with the x-ray diffraction method. Based on these spectroscopic data, it was concluded that this Rh complex can be called a stereoregular polymerization catalyst of alkyl propiolate because the poly(alkyl propiolate) obtained has a cis-transoidal structure.

INTRODUCTION

In our previous reports [1, 2] the highly stereoregular polymerization of phenylacetylene derivative and the living polymerization of *m*-chlorophenylacetylene have been shown to be induced by [Rh(norbornadiene)Cl]$_2$, [Rh(NBD)Cl]$_2$, catalyst when either triethylamine (TEA) or chloroform was used as the polymerization solvent. Poly(phenylacetylene)s with the *p*-methoxy, *p*-methyl, and *m*-chloro groups in the phenyl ring were obtained in fairly high yields, where polymers with a cis-transoidal structure were formed stereospecifically. However, there are no reports to date on the polymerization of alkyl propiolates catalyzed by the Rh complex as the highly stereoregular polymerization catalyst. Therefore, it is of interest to investigate whether the stereoregular polymerization of alkyl propiolate is induced by the Rh complex. It is worth mentioning that poly(alkyl propiolate) polymer has several potential advantages for industrial applications because of recent expectations that such a π-conjugated polymer will exhibit photo- and electrical conductivity, magnetic properties, and oxygen permeability.

In this study we describe the first stereoregular polymerization of alkyl propiolate by a Rh base catalyst, e.g., $[Rh(NBD)Cl]_2$, together with the characterization of its resulting poly(alkyl propiolate) using IR, ^{13}C-NMR, CP MAS ^{13}C-NMR, laser Raman spectroscopies, and the x-ray diffraction method.

EXPERIMENTAL

Methyl, ethyl, and *t*-butyl propiolates (from Tokyo Chemical Industry Co.) were used after distillation under reduced pressure. Normal butyl, isobutyl, *n*-octyl, and *l*-menthol propiolate were prepared by heating the corresponding alcohol and propiolic acid together in the presence of *p*-toluene sulfonic acid as a dehydration catalyst [3] and distillated before use.

$[Rh(NBD)Cl]_2$ and $[Rh(COD)Cl]_2$ (from Aldrich), $[Rh(COD)\{P(Ph)_3\}_2]PF_6$ and $RhCl_3 \cdot 3H_2O$ (from Wako Chemicals), and an organometallic cocatalyst were commercially obtained and used without further purification.

General Procedure of Polymerization

Polymerization was carried out using a specially designed U-type ampule, where two glass inlets with septum caps at the tops of the tube were installed. The Rh catalyst was placed in one side arm in the ampule and monomer solution was introduced from the other side arm with the aid of a hypodermic syringe under a dry nitrogen atmosphere. The solvents used, including methanol, tetrahydrofuran (THF), toluene, and dichloromethane, were dried before use according to the conventional method. The polymerization was carried out at 40°C for 24 hours. The polymers formed were isolated by precipitation in a large amount of methanol. All the polymers that precipitated were filtered off and dried under reduced pressure at 40°C at $\sim 10^{-3}$ torr. Polymer yield was measured by gravimetry. Molecular weights were measured by gel permeation chromatography (GPC) with a polystyrene standard.

^{13}C-NMR spectra were recorded on a Jeol GX 270 in $CDCl_3$ solution, and the solid ^{13}C-NMR spectrum was observed on a Bruker MSL 400 spectrometer with a CP MAS unit. The resonance Raman (RR) spectra were measured on a Jeol 400T triple monochrometer model after compression of polymer on a KBr disk at the excitation wavelength of an argon laser at 514.5 nm. Wide-angle x-ray diffraction analysis was performed on a Rigaku Denki 2142 model.

RESULTS AND DISCUSSION

Polymerization of Alkyl Propiolate

Table 1 lists the results for the polymerization of methyl propiolate by $[Rh(BND)Cl]_2$ catalyst in various solvents. Methyl propiolate was polymerized effectively, i.e., the yield reached ~70% when the polymerization was carried out for 24 hours in methanol as the polymerization solvent.

However, THF, toluene, and dichloromethane were not effective solvents for polymerization. This finding is interesting when compared with those of the other monomers; THF and toluene were active solvents for the polymerization of phenylacetylene initiated by the $[Rh(NBD)Cl]_2$ catalyst [2]. It is known that methanol, when used as a solvent, works as a dissociator of the binuclear complex $[Rh(NBD)Cl]_2$ to generate the monomeric form Rh(NBD)Cl-solvent, which has been suggested as the precursor of the propagation species in this polymerization [1, 2]. Thus, methanol was the preferred solvent.

The resultant poly(methyl propiolate) polymer was a pale yellow powder and insoluble in common organic solvents. This is notably different compared with poly(methyl propiolate) produced by the catalyst $MoCl_5$ [4]. This polymer, obtained in 27% yield, was soluble in organic solvents and had a gray color. No other alkyl propiolate except methyl propiolate was polymerized by the $MoCl_5$ catalyst. The difference in solubility observed may be due to the polymer structure formed, as later suggested by the x-ray diffraction method.

Table 2 lists the results for the polymerization of methyl propiolate by Rh-based catalysts. $[Rh(NBD)Cl]_2$ catalyzed the polymerization most effectively, i.e., the polymer yield was 80% when the polymerization was performed in methanol at 40°C for 48 hours.

It is interesting to see how the bulkiness in the alkyl group of the alkyl propiolate monomer affects the yield and molecular weight. As Table 3 shows, the more bulky alkyl group in the monomer reduced the yield compared with the smaller alkyl group in the monomer (see Table 3, No. 2 and 3, 6 and 7, 6 and 8) together

TABLE 1. Polymerization of Methyl Propiolate by $[Rh(NBD)Cl]_2$ in Various Solvents[a]

No.	Catalyst	Solvent	Time, h	Polymer yield,[b] %
1	$[Rh(NBD)Cl]_2$	CH_3OH	24	70
2	"	CH_3COOH	24	2
3	"	THF	24	11
4	"	Toluene	24	13
5	"	CH_3CO_2Et	24	11
6	"	CH_2Cl_2	24	13

[a] Polymerized at 40°C. $[M]_0$ = 2 mol/L, [catalyst] = 20 mmol/L.
[b] Insoluble fraction in methanol.

TABLE 2. Polymerization of Methyl Propiolate by $[Rh(NBD)Cl]_2$ in Methanol[a]

No.	Catalyst	Temperature, °C	Time, h	Polymer yield,[b] %
1	$[Rh(NBD)Cl]_2$	40	48	80
2	"	40	24	70
3	$[Rh(COD)Cl]_2$	40	24	23
4	$[Rh(COD)\{P(Ph)_3\}_2]PF_6$	40	24	9
5	$RhCl_3 \cdot 3H_2O$	40	24	0

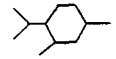
[a] Polymerized at $[M]_0 = 2$ mol/L, [catalyst] = 20 mmol/L.
[b] Insoluble fraction in methanol.

with a decrease of molecular weight. This may be explained in terms of the degree of molecular crowding around the Rh center at the propagation stage.

The effect of alcohol as a polymerization solvent was studied (Table 3). Normal butyl propiolate produced a 61% polymer yield when methanol was used. However, higher alcohols (e.g., *n*-butyl alcohol) produced a higher yield. Thus, higher alcohols seem to work as more effective solvents for this polymerization. This may be attributable to an increase in the solubility of the polymer by the solvent while maintaining a homogeneous solution.

Ph_3Sn, an organometallic compound, was found to be an ineffective cocatalyst although it has been used as the cocatalyst for polymerization of *o*-substituted phenylacetylenes by $MoCl_5$ or WCl_6 catalyst [5] (Table 3, No. 4).

TABLE 3. Polymerization of Alkyl Propiolate by $[Rh(NBD)Cl]_2$ Catalyst[a]

No.	Monomer HC≡CCOOR	Solvent	Catalyst	Yield, %	MW
1	CH_3	MeOH	$[Rh(NBD)Cl]_2$	70	—
2	CH_3CH_2	MeOH	$[Rh(NBD)Cl]_2$	63	35,000
3	*n*-C_4H_9	MeOH	$[Rh(NBD)Cl]_2$	61	18,000
4	*n*-C_4H_9	MeOH	$[Rh(NBD)Cl]_2 \cdot Ph_3Sn$	57	15,000
5	*n*-C_4H_9	EtOH	$[Rh(NBD)Cl]_2$	49	19,500
6	*n*-C_4H_9	*n*-BuOH	$[Rh(NBD)Cl]_2$	73	83,600
7	*i*-C_4H_9	*n*-BuOH	$[Rh(NBD)Cl]_2$	65	30,100
8	*t*-C_4H_9	*n*-BuOH	$[Rh(NBD)Cl]_2$	25	7,800
9	*n*-C_8H_{17}	*n*-BuOH	$[Rh(NBD)Cl]_2$	76	48,600
10		MeOH	$[Rh(NBD)Cl]_2$	45	13,400

[a] Polymerized at 40 °C for 24 hours. $[M]_0 = 2$ mol/L, [catalyst] = 20 mmol/L.

It is known that a strained ligand such as norbornadiene in the Rh of the $[Rh(NBD)Cl]_2$ complex strongly coordinates to the Rh metal center to produce a more stable complex compared with the cyclooctadiene ligand in the $[Rh(COD)Cl]_2$ complex which more loosely coordinates to the Rh center [6]. Therefore, COD in $[Rh(COD)Cl]_2$ may be replaced with other molecule-like solvents during polymerization, as has been reported [6]. This replacement of the weakly coordinated ligand may induce the decomposition of the initiation or propagation species of the $[Rh(COD)Cl]_2$ catalyst, giving lower polymerization yields. Polymerization with $RhCl_3 \cdot 3H_2O$ resulted in no yield.

Properties and Structures of Polymers

The elemental composition of all polymers agreed with the theoretical one, e.g., for poly(methyl propiolate): C, 57.14%; H, 4.80%. Found: C, 57.32%; H, 4.80% (sample: Table 1, No. 1).

Poly(methyl propiolate), obtained as a pale yellow powder, was quite stable in the air for 2 years at room temperature, although it is known that polyacetylene is gradually oxidized in the air. The carbonyl group as an oxidized product was detected by IR and NMR spectroscopy [7]. Insolubility of poly(methyl propiolate) polymerized by the Rh complex catalyst suggests that the resulting polymer does not have a planar structure but rather a helical one with a narrow helical pitch width, by which solvents such as chloroform or toluene are prevented from coordinating to solvate the polymer chain as suggested in our previous paper [2]. This insolubility may be correlated with the strong van der Waals interactions between the delocalized π-electron cloud on the adjacent polymer chain. On the other hand, poly(propiolates) involving alkyl groups other than methyl in the ester moiety were found to be soluble in common solvents. When the molecular weight distribution of such soluble poly(propiolate) polymers was measured by GPC, utilizing a polystyrene standard, the polydispersity (M_n/M_w) was estimated as 2-6. The wide dispersity observed was different from that for the case of the polymerization of *m*-chlorophenylacetylene by the Rh-based catalyst where the living-like polymerization gave rise to a rather narrow molecular weight distribution [1].

Figure 1 shows the IR spectrum of poly(methyl propiolate) synthesized by $[Rh(NBD)Cl]_2$ catalyst. Absorptions at 2200-2100 cm^{-1} due to C≡C stretching and at 3200 cm^{-1} due to ≡CH were not observed in the spectra of all polymers, thus indicating the absence of a monomer in the polymer. The poly(alkyl propiolate) polymer showed bands at 3050 cm^{-1} (=CH), 2950-2850 cm^{-1} (CH_3), 1730-1720 cm^{-1} (C=O), 1620 cm^{-1} (conjugated double bond), and 1250-1200 cm^{-1} (C—O).

Figures 2(a) and 2(b) show the CP MAS ^{13}C-NMR spectrum of insoluble poly(methyl propiolate) in the solid state and the ^{13}C-NMR spectrum of poly(ethyl propiolate) observed in $CDCl_3$, respectively. The CP MAS ^{13}C-NMR spectrum was found to consist of the following signals: 52.0 ppm ($-OCH_3$), 128 ppm (=CH), 134 ppm (=C—), and 164 ppm (C=O). These signals suggest that the resulting polymer also has the cis-transoidal structure shown in Fig. 3, as pointed out in our previous report [8].

It was previously reported by Masuda et al. [4] that poly(methyl propiolate) polymerized by $MoCl_5$ was soluble and has a gray color although the polymer

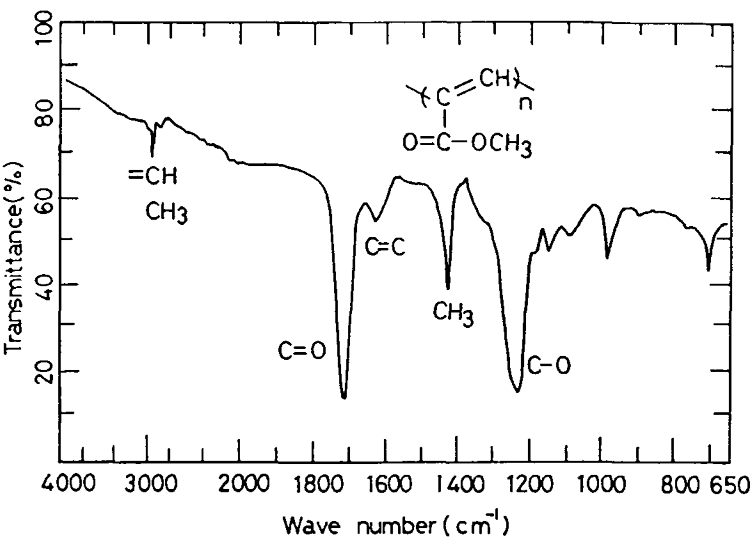


FIG. 1. Infrared spectrum of poly(methyl propiolate) polymerized by $[Rh(NBD)Cl]_2$ catalyst in methanol at 40 °C.

synthesized by a Rh catalyst is pale yellow and insoluble. Such a difference may be due to the structure of the polymer, because the soluble polymer synthesized with $MoCl_5$ may be composed of a mixture of cis and trans chain sequences in the conjugated backbone. Therefore, the irregularity of the chain sequence in the conjugated backbone may enhance solubility.

Figure 4 shows the laser Raman spectra of poly(methyl propiolate) and poly(ethyl propiolate) polymers. We carried out the spectral assignment because to this date no Raman data have been published on poly(alkyl propiolate) to our knowledge. A broad peak with a shoulder was observed at 1535 cm^{-1}. This broad peak may be assigned to the C=C stretching mode in the cis polymer, as reported in the case of simple polyacetylene [9]. The peak at 1230 cm^{-1} with a shoulder may also be attributable to the C—C stretching mode with a considerable addition of C—H deformation in-plane in *cis*-polyacetylene. The peak at 1535 cm^{-1} has a wide shoulder in the higher wavenumber region. The observed broad peaks corresponding to the C=C bond may be explained in terms of double bonds with various conjugated lengths in poly(methyl propiolate) synthesized with Rh complex, in analogy with polyacetylene as previously reported [9].

On the other hand, we found that the shoulder of the peak at 1535 cm^{-1} was observed in the cases of poly(ethyl propiolate) polymers. This suggests that the width of the chain sequence distribution of conjugated double bonds is also not narrow. A very weak signal due to the C=O group was also observed at 1720 cm^{-1}. The band at 1360 cm^{-1} may arise from the in-plane deformation of the single hydrogen atom in C=C—H [10]. Thus, the Raman spectral data support the belief that poly(alkyl propiolate) synthesized by the Rh complex also consists of the cis-transoidal structure.

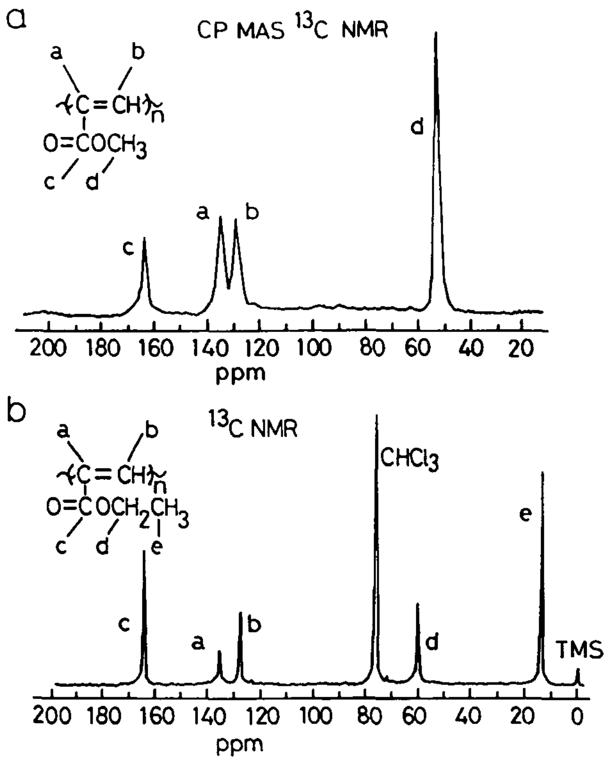


FIG. 2. NMR spectra of poly(alkyl propiolate) polymers. (a) ^{13}C-NMR spectrum observed by the CP MAS method from the insoluble poly(methyl propiolate) solid polymerized by $[Rh(NBD)Cl]_2$ catalyst in methanol. (b) ^{13}C-NMR spectrum observed in $CDCl_3$ from the poly(ethyl propiolate) polymerized by $[Rh(NBD)Cl]_2$ catalyst in methanol.

X-Ray Analysis

X-ray analysis of the poly(alkyl propiolate) obtained was carried out to determine whether these polymer are amorphous. As Fig. 5 shows, the poly(methyl propiolate) polymer showed crystalline peaks at 2θ = 10.1 and 18.1°, and an amor-

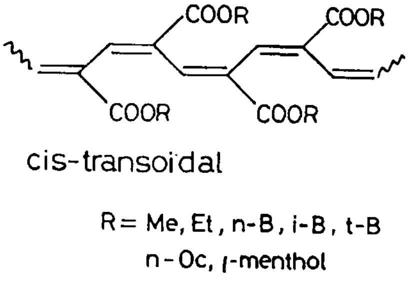


FIG. 3. Cis-transoidal conformer of poly(alkyl propiolate).

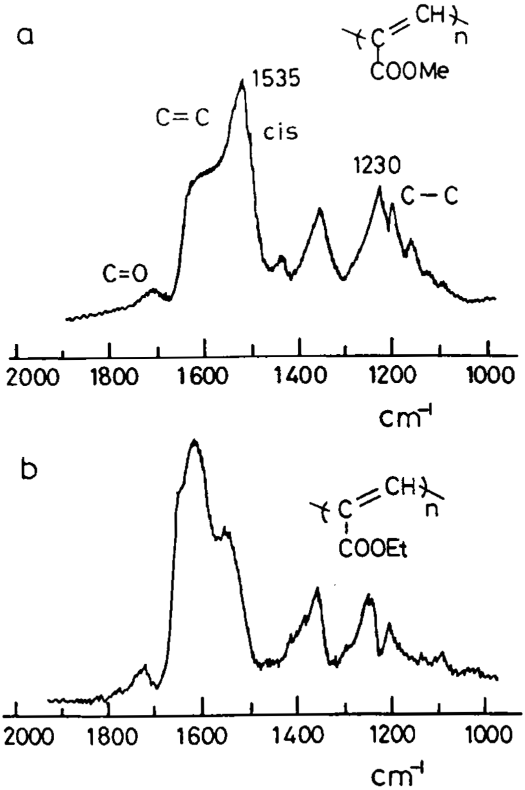


FIG. 4. Laser Raman spectra of poly(alkyl propiolate) polymerized by $[Rh(NBD)Cl]_2$ catalyst in methanol. (a) Poly(methyl propiolate). (b) Poly(ethyl propiolate).

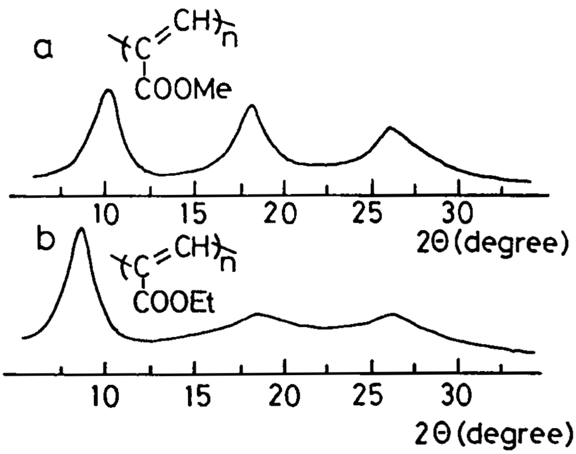
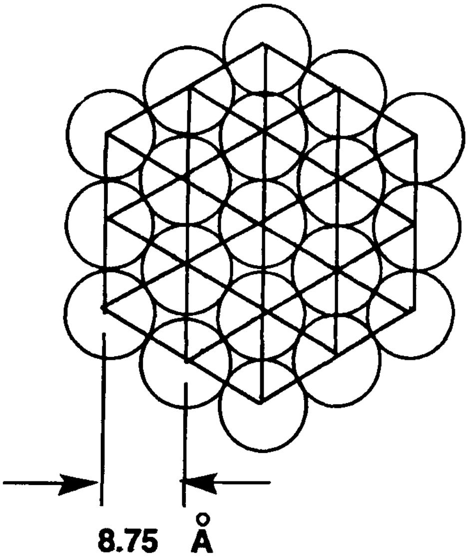


FIG. 5. Typical x-ray diffraction spectra of poly(alkyl propiolate) polymerized by $[Rh(NBD)Cl]_2$ catalyst in methanol. (a) Poly(methyl propiolate). (b) Poly(ethyl propiolate).

phous halo at 26.2°. The degrees of crystallinity of poly(methyl propiolate) and poly(ethyl propiolate) were estimated to be ~56 and 27%, respectively.

It should be noted that the peak positions at 18.1 and 26.2° remained nearly constant even when the methyl group in poly(alkyl propiolate) was replaced by the more bulky ethyl group. On the other hand, the peak at the lowest angle side, 10.1°, was found to shift to the smaller angle side, i.e., ~8.7°. This shift may be interpreted as an increase of the intermolecular distance of the main chain, i.e., the diameter of the helical polymer chain, suggesting the formation of a pseudohexagonal crystal structure such as that found in a rigid and rodlike molecule. Such a rodlike polymer also was conjectured through a modified force field calculation for poly(phenylacetylene) [11]. The lateral spacings from the diffraction patterns for poly(alkyl propiolate) with methyl and ethyl groups were estimated as 8.75 and 10.15 Å, respectively, which can be interpreted as the $(10\bar{1}0)$ diffractions of the pseudohexagonal arrays [12]. The hexagonal packing of the rodlike molecule in the case of poly(methyl propiolate) is shown below.



This assumption is not unreasonable because the molecular volume of the ethyl group is larger than that of the methyl group. The peak at $2\theta = 18.1°$ may be evidence for an ordered distance (i.e., 4.92 Å) along the chain axis as in the case of poly(*N*-vinylcarbazole) [13]. Such polymers with a pseudohexagonal structure are known [12, 14]. A more detailed x-ray study on the crystal structure is in progress.

CONCLUSION

The polymerization of alkyl propiolate was studied with the Rh complex catalyst which is known as a stereoregular polymerization catalyst for aromatic acetylenes. Consequently, poly(alkyl propiolate)s were also obtained in relatively high yield, 80%, when alcohol was used as the polymerization solvent at 40°C. The characterization of the structure of the polymer obtained by this catalyst was carried out using conventional spectroscopic methods, including solution and solid ^{13}C NMR, laser Raman spectroscopic methods, along with the x-ray diffraction method. Based on the spectroscopic data of the resulting polymers, it was concluded that poly(alkyl propiolate) has the cis-transoidal structure.

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