Structural Differences between Polypentynoates Bearing Mesogenic Moieties Polymerized with RH Complex and WCl$_6$ Catalysts. A ^{13}C-NMR and Raman Study

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STRUCTURAL DIFFERENCES BETWEEN POLYPENTYNOATES BEARING MESOGENIC MOIETIES POLYMERIZED WITH Rh COMPLEX AND WCl$_6$ CATALYSTS. A ^{13}C-NMR AND RAMAN STUDY

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ABSTRACT

Pentynoates containing mesogenic groups, i.e., HC≡CCH$_2$CH$_2$-COOR (R = dihydrocholesteryl and p-methoxybiphenyl) were stereo-regularly polymerized using a Rh complex catalyst, [Rh(norbornadie-ne)Cl]$_2$, in the presence of triethylamine as the cocatalyst. The structure of the polymer obtained was compared with that of an analogous poly-mer prepared using the metathesis catalyst WCl$_6$ in dioxane by ^{13}C-NMR and laser Raman spectroscopic methods. The data indicated that the polypentynoate polymerized with the Rh complex has a cis-transoid form which allowed us to observe the two clear carbon signals C=CH of the main chain in the ^{13}C-NMR spectrum. The polypentynoate prepared using the WCl$_6$ catalyst was found to have the trans-transoid conjugation length with $N_{C=C} \approx 7$, which did not allow observation of the clear carbon signals of the main chain in the ^{13}C-NMR spectrum.

INTRODUCTION

In previous papers [1, 2] we have shown that the polymerization of phenyla-cetylene and its homologues and alkyl propiolate, $HC \equiv CCOOR$, catalyzed by the Rh complex, i.e., [Rh(norbornadiene)Cl]$_2$, [Rh(NBD)Cl]$_2$, in organic solvents such as triethylamine (TEA) or alcohol selectively gives highly stereoregular cis-trans-oidal polymers with helical structures in very high yields. In addition, we have also shown that the Rh complex catalyst quantitatively produces an ultrahigh molecular weight polyphenylacetylene (UHMW PPA), $M_w \approx 4.42 \times 10^6$ [3].

The triethylamine (TEA) used as an organic base was thought to be involved in the reaction by promoting the dissociation of the bidentate complex, [Rh(NBD)Cl]$_2$, into the monomeric species which, in turn, may be an important initiation species for this polymerization [4] as shown in Scheme 1. In addition, we also found that the Rh complex initiated the living polymerization of m-chlorophenylacetylene in triethylamine [1].
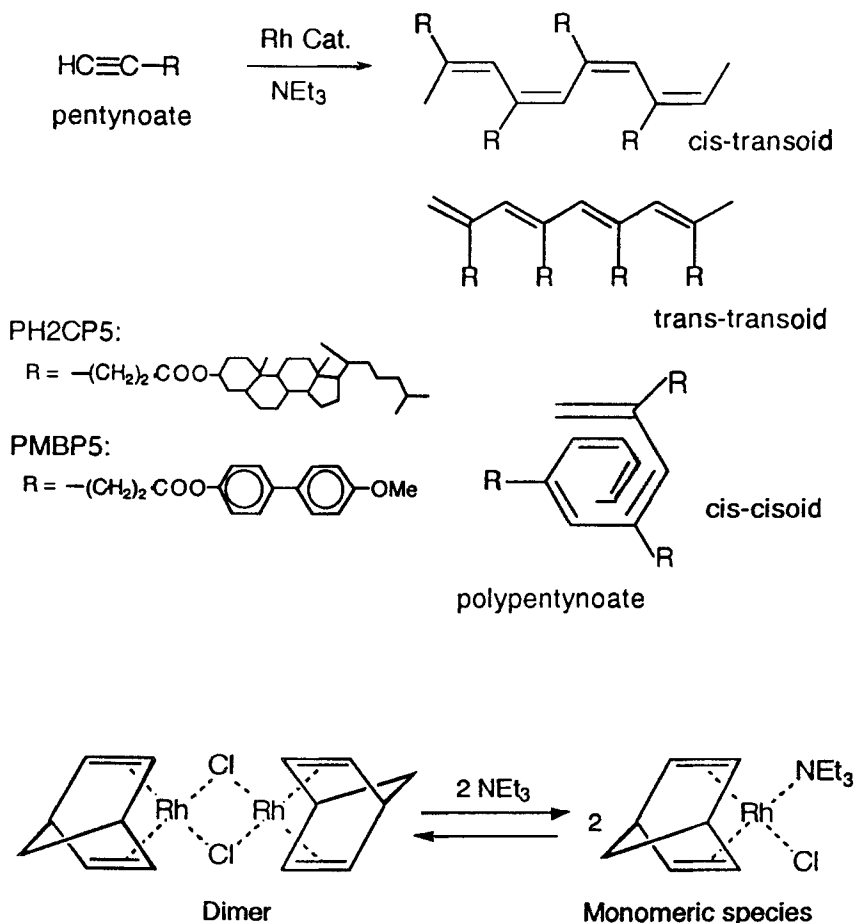
SCHEME 1.

Based on x-ray analyses of poly(alkylpropiolate) polymers polymerized by the Rh complex, it was concluded that the polymer has a pseudohexagonal packing crystal structure in the solid state where the helical chain having a rigid rodlike structure is formed [2].

Recently, polymerizations of aliphatic acetylene monomers with liquid crystal properties were performed with not only a metathesis catalyst, WCl_6 [5, 6], but also with a Ziegler–Natta catalyst [6]. However, the geometrical structures, e.g., cis and trans forms with respect to the double bond in the resulting polyacetylene liquid crystals, have not yet been investigated in detail by unequivocal spectroscopic methods, e.g., NMR and/or Raman methods, although the properties of liquid crystals are dependent on the geometrical structures of the polymers. It should be noted that polyacetylene liquid crystals are important for industrial applications because such a π-conjugated polymer would be expected to exhibit photo and electrical conductivities [7], magnetic properties [8, 9], nonlinear optical (NLO) properties [10], and oxygen permeable properties [11, 12].

In this report we describe the first stereoregular polymerization of the esters of pentynoic acid bearing a dihydrocholesteryl or 4-methoxybiphenyl group as the mesogen, and methylene chains as the spacer. The reaction was induced by the $[Rh(NBD)Cl]_2$ catalyst in TEA as the solvent. Further, the structural assignments and differences between the polypentynoates, PH2CP5-Rh and PH2CP5-W polymers, produced by the Rh complex and metathesis catalyst, WCl_6, will be shown using solution and solid ^{13}C-NMR and laser Raman spectroscopic methods together with an estimation of the conjugation length of polymers obtained.

EXPERIMENTAL

Synthesis

Dihydrocholesteryl pentynoate (H2CP5) was prepared as follows: 25.5 mmol (9.91 mg) of dihydrocholesterol (Tokyo Chemical Ind.) and 30 mmol (2.94 mg) of pentynoic acid (Tokyo Chemical Ind.) were reacted with 28 mmol (5.78 mg) of dicyclohexylcarbodiimide (DCC) (Tokyo Chemical Ind.) and 0.12 mmol (150 mg) of N,N-dimethylaminopyridine (DMAP) (Tokyo Chemical Ind.). The ester was purified by silica gel column chromatography with $CHCl_3$ as eluent and was obtained as white crystals. Yield, 70%; mp, 121°C; IR, 3300 cm^{-1} (C—H), 2180 cm^{-1} (C≡C), 1720 cm^{-1} (C=O), 1195 cm^{-1} (C—O), 1285 cm^{-1} (C—O); ^1H NMR ($CDCl_3$), 1.95 ppm (s, 1H, ≡C—H), 2.50 ppm (m, 4H, CH_2CH_2). Calculated: C 81.99%, H 11.18%; found: C 82.02%, H 11.22%.

4-Methoxybiphenyl-4'-pentynoate (MBP5) was obtained by reaction of 13.9 mmol (1.37 g) of pentynoic acid and 12.5 mmol (2.50 g) of 4-methoxy-4'-hydroxybiphenyl (Tokyo Chemical Ind.) with 12.5 mmol (2.58 g) of dicyclohexyl-carbodiimide (DCC) and 0.57 mmol (70 mg) of N,N-dimethylaminopyridine (DMAP). Purification was done by silica gel column chromatography with $CHCl_3$ as eluant to give white crystals. Yield, 70%; mp, 110°C; IR, 3270 cm^{-1} (≡C—H), 2280 cm^{-1} (C≡C), 1745 cm^{-1} (C=O), 1280 cm^{-1} (C—O), 1140 cm^{-1} (C—O), 810 and 840 cm^{-1} (1,4 disubstituted); ^1H NMR ($CDCl_3$), 2.04 ppm (s, 1H, alkenyl),

2.77 ppm (m, 4H, CH_2CH_2). Calculated: C 77.12%, H 5.75%; found: C 6.97%, H 5.89%.

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, $[Rh(NBD)Cl]_2$ (Aldrich), 0.056 mmol (13 mg), was placed in one side arm of the ampule and 2.1 mmol (1.0 g) of monomer was introduced from the other side arm with the aid of a hypodermic syringe in an atmosphere of dry nitrogen. The solvent, i.e., dioxane (7 mL), dried over CaH_2, or triethylamine (TEA) (7 mL), dried by refluxing with benzophenone and sodium wire, was introduced from both side arms to give homogeneous solutions. Polymerization reactions were run at 40°C for 24 hours. The resulting polymer solutions were poured into a large excess of methanol (50 mL), and the precipitated polymer was isolated on a filter. Hot methanol was used to extract the resulting cyclic trimer during the polymerization, and the purified polymer was dried under reduced pressure at $\sim 10^{-3}$ torr at 40°C for 24 hours. Polymer yields were estimated gravimetrically. Molecular weights were measured by gel permeation chromatography (GPC) using tetrahydrofuran as the eluant, and Asahipac columns GS-310 and GS-510 with a polystyrene standard.

^{1}H-NMR and ^{13}C-NMR spectra were run on a Jeol EX 400 MHz spectrometer in $CDCl_3$ solution with tetramethylsilane (TMS) as a standard signal at 30°C. The solid-state ^{13}C-NMR spectrum was observed using a Bruker MSL 360 MHz spectrometer with a CP MAS unit where the TOSS technique was used to delete spinning side bands [13].

Laser Raman spectra were run on a Renishaw FT Ramascope S2000 with the excitation wavelengths of He-Ne laser light at 637.4 nm. UV spectra were observed with a Shimadzu model 210 instrument using tetrahydrofuran as solvent.

RESULTS AND DISCUSSION

Table 1 lists the results of polymerization of the acetylene esters, i.e., pentynoates which were catalyzed by the Rh complex in TEA and the WCl_6 metathesis catalyst in dioxane.

TABLE 1.   Polymerization Results of Acetylene Esters Produced by $[Rh(NBD)Cl]_2$ Catalyst and Metathesis Catalyst, WCl_6[a]

No.	Monomer	Catalyst/solvent	[Catalyst]:[M]	Yield, %	M_n[b]
1.	PH2CP5	$[Rh(NBD)Cl]_2$/TEA	1:40	67	58,000
2.	PH2CP5	WCl_6/dioxane	1:40	62	20,000
3.	PMBCP5	$[Rh(NBD)Cl]_2$/TEA	1:40	31	—[c]
4.	PMBCP5	WCl_6/dioxane	1:40	73	20,000

[a]Polymerized at 40°C for 24 hours. [M] = 2.1 mol/L.
[b]Estimated by GPC using polystyrene standards in chloroform.
[c]Insoluble.

The yield of the dihydrocholesteryl pentynoate polymer, PH2CP5, was approximately 67% with $M_n \approx$ 58,000. These polymers were soluble in chloroform, benzene, and tetrahydrofuran, but insoluble in methanol, n-hexane, acetone, and diethyl ether. The molecular weight dispersities, M_w/M_n values of the polypentynoates which were obtained as soluble polymers, were estimated as ca. 2–4 using polystyrene standards.

The polymerizations of 4-methoxybiphenyl-4′-pentynoate (MBP5) were also performed using the Rh complex in TEA solvent and WCl_6 in toluene. The yields of the resulting PMBP5-Rh and PMBP5-W polymers were 31 and 73%, respectively. The resulting PMBP5-Rh polymer was insoluble in ordinary solvents, but the PMBP5-W polymer was soluble in THF, chloroform, and toluene. Thus these results indicate that the polymerization of the pentynoate with the dihydrocholesteryl mesogen and ethyl group as the spacer can be induced by the Rh complex and also by the WCl_6 catalyst.

It is noteworthy that simple alkyl acetylenes such as 1-hexyne, which does not possess an ester group at the end of a normal alkyl chain, were not reactive and did not polymerize in the presence of the Rh complex, even when the most active cocatalyst, triethylamine, was used [14].

¹³C-NMR Spectra

Figures 1(a) and 1(b) show the ¹³C-NMR spectra of PH2CP5-Rh and PH2CP-W polymers observed in CDCl₃ solutions at 30°C, respectively. The spectrum of the PH2CP5-Rh polymer is classified into two chemical shift regions: one is an aliphatic carbon signal region at the higher field side from ca. 10–70 ppm and the other is an unsaturated carbon signal region from ca. 120–180 ppm. The higher field signals are assigned to the typical cholesteryl carbons and methylene spacer carbons. The lower field signals can be assigned to the main chain carbons except for the carbonyl carbon signal at 163 ppm. The peaks at 127.0 ppm are assigned to the tertiary carbons, H—C=, in the main chain and those at 139.2 ppm to the quaternary carbons, =C=, in the main chain as reported by us for the case of poly(n-alkylpropiolate) polymer [2]. The ¹³C-NMR spectrum of the PH2CP5-W polymer was compared with that of the PH2CP5-Rh polymer. Figure 1(b) shows the ¹³C-NMR spectra of the PH2CP5-W polymer observed in CDCl₃ solution at 30°C where the expanded chemical shift portion of the C=C bond is inset as Fig. 1(b) with that of the PH2CP5-Rh polymer. As can be seen in Fig. 1(b), the two peaks at 127.0 and 139.2 ppm, which are expected for the main chain carbons, were not clearly observed, unlike that of the PH2CP5-Rh polymer. Only small, barely visible peaks are seen. Thus, it is difficult to unequivocally assign the geometrical structures in the PH2PC5-W polymer because no clear signals corresponding to the carbons, i.e., =C= and HC=, in the main chain can be observed. It is also noteworthy that these signals disappeared when the temperature was raised from 30 to 70°C. These results lead us to conclude that the Rh complex is the preferred catalyst for the assignment of the signals of the two main chain carbons even in aliphatic polyacetylene esters, suggesting that the Rh complex is a stereoregular polymerization catalyst for the pentynoate monomers, giving polypentynoate polymers having a cis-transoid form as we previously reported [1–4]. It should also be noted here that a similar difference in the ¹³C-NMR spectra between the polypentynoates polymerized with
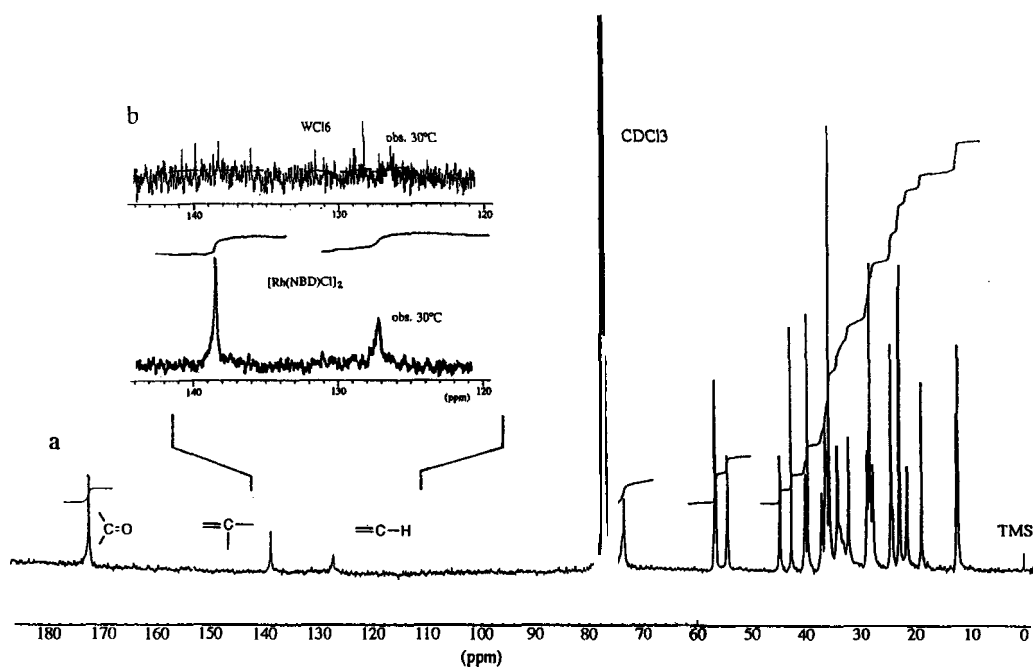
FIG. 1. ^{13}C-NMR spectra of poly(dihydrocholesteryl pentynoate) polymer, PH2CP5 observed in CDCl$_3$ solution at 30°C. (a) Polymerized with Rh complex in triethylamine. (b) Polymerized with WCl$_6$ in dioxane.

Rh complex and WCl$_6$ catalysts has been reported for the case of polyphenylacety-lene [15].

It appears that the metathesis catalysts, such as WCl$_6$, may not always give rise to polymers with regular structures, i.e., head-to-tail structure, but with an irregular structure, i.e., head-to-head and/or tail-to-tail structure, which was incorporated in the main chain of the polyacetylene as has been suggested [4, 16]. Therefore, such a structural irregularity introduced in the main chain carbons makes the spectral assignments difficult. In addition, thermal cis-trans isomerization during and/or after the polymerization takes place and the resulting trans sequences must be incorporated in the cis main chain, then the molecular motion of the main chain may become slower and the main chain becomes stiff due to formation of the extended trans sequence. Therefore, an increase in the linewidth of the NMR spectra may be interpreted in terms of the statistically wide distribution for the chemical shifts. In addition, some cyclization of the main chain may also take place, produc-ing a cyclohexadienyl moiety giving different relaxation times in each carbon as has been reported in the polymerization of phenylacetylene [4, 16]. Thus, if molecular motion of the main chain is reduced by such irregular structures, the main chain carbons may have a wide chemical shift distribution and/or a diffuse relaxation time by which the weak and/or complex signals may be observed as shown in Fig. 1(b).

On the other hand, the PH2CP5-Rh polymer appears to have a highly regular head-to-tail structure with a cis-transoid form. Such a polymer would be expected

to have a fairly narrow distribution of chemical shifts and/or no diffuse relaxation time, producing the clear signals of the main chain carbons as shown in Fig. 1(a).

An alternative explanation for the spectrum observed in the PH2CP5-W polymer is that it may be due to the magnetic dipole–dipole interactions between the radical and proton spins in the polymer where the linewidth broadening of each signal usually takes place [17]. Radical spins are thought to be produced by isomerization from the cis to the trans form during polymerization and/or after polymerization, where the double bond in the cis form must be broken to generate two radical spins per one double bond as a biradical, as has been suggested [4, 9, 18] and where the spin was called a soliton [19, 20]. Thus it is necessary to bear in mind that the double bond signals of the polypentynoate polymers polymerized by a metathesis catalyst, such as WCl_6, are not always observable due to the complex effects mentioned above.

Poly(4-methoxybiphenyl-4′-pentynoate), a PMBP5-Rh polymer polymerized with Rh complex, was insoluble in ordinary solvents, but the PMBP5-W polymer was soluble only in solvents such as benzene, chloroform, and tetrahydrofuran. Therefore, the CP MAS ^{13}C-NMR spectrum of the PMBP5-Rh polymer was measured at room temperature using the TOSS technique to avoid the appearance of spinning side bands where the intensity of each peak was unreliable [13]. Figure 2 shows the CP MAS ^{13}C-NMR spectrum of PMBP5-Rh polymer. The signals observed at ca. 138 and 127 ppm were assigned to the quaternary ($=C=$) and tertiary ($=CH$) carbons in the main chain, respectively, although the latter peak was superimposed with those of the biphenyl carbons. The signal at 166 ppm was assigned to the carbonyl carbon, and the signals at 34 and 55 ppm can be attributed to the two methylene and methoxy carbons, respectively. Therefore, these results suggest that the resulting polymer also has the cis-transoid form shown in Scheme 1. The insolu-
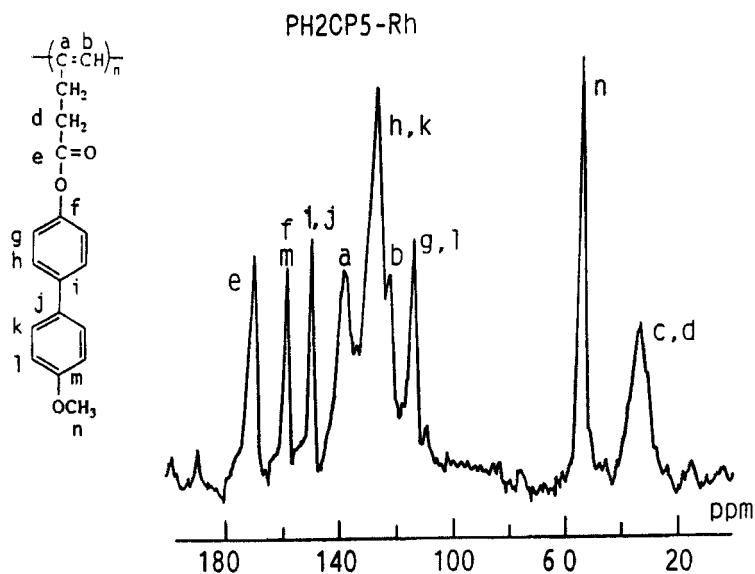

FIG. 2.   CP MAS ^{13}C-NMR spectrum of PMBP5 polymer observed at 25°C.

bility of the PMBP5-Rh polymer may not be due to crosslinks between molecular chains and/or side reactions making some inter- and/or intracovalent bonds but, rather, to the helicoidal structure. The PMBP5-Rh polymer can be considered to have a very high cis transoid and/or cis cisoid content; in other words, a high regularity as the major structure without a significant irregular structure, e.g., trans sequence. Therefore, such polymer may not be sufficiently solvated to dissolve due to the rather narrow helical pitch width. In our previous papers [2–4] similar cases were reported in the polymers of poly(methylpropiolate), PMP, as well as of poly(p-methylphenylacetylene), PMPA, and poly(p-chlorophenylacetylene), PCPA, all of which were polymerized using the Rh complex. These polymers are soluble, however, when they are prepared using the WCl_6 catalyst instead of the Rh complex. Recently we found that the above polymers have pseudohexagonal crystal structures, i.e., a so-called columnar structure packed with the helicoidal polymer chain [2].

On the other hand, the ^{13}C-NMR spectrum of the PMBP5-W and PH2CP5-W polymers did not show any main chain carbon signal in $CDCl_3$ solution at room temperature, indicating that metathesis catalysts, such as WCl_6, is not always suitable for deducing the geometrical structure of the resulting polyacetylene.

Raman Study

Raman spectra of the conjugated polymers have been used to determine the geometrical structure with respect to the double bond and to estimate the sequence length of the double bonds in polyacetylenes [2, 8c, 21]. The exact band position in the Raman spectra is sensitive to the degree of the length of the conjugated double bonds system in polyacetylenes and the excitation wavelength employed. Therefore, the sequence length can be estimated if the suitable laser wavelength is used. This technique is referred to as resonance Raman (RR). We observed the RR spectra of PH2CP5-Rh and PH2CP5-W polymers using an excitation laser wavelength, i.e., He-Ne laser of 637.4 nm, in order to determine the polymer structure and estimate the sequence length of the double bond of both PH2CP5 polymers. The results are shown in Fig. 3. The large peaks observed at ca. 2800 cm^{-1} were assigned to those of the alkyl groups (CH_3, CH_2, and CH groups) in the dihydrocholesteryl skeleton and spacer [22], although the peaks of the aliphatic groups were omitted.

The stretching bands at 2200 and 3200 cm^{-1} due to the C≡C bond and C—H bond in the ≡C—H moiety, respectively, were not observed in the PH2CP5 and PMBP5 polymers, indicating the absence of their monomers, although the aliphatic bands in excess of 1800 cm^{-1} were omitted from the spectra. The small band at 1720 cm^{-1} in each spectrum was attributed to the C=O bond in the ester group.

The band at 1618 cm^{-1} observed in the PH2CP5-Rh polymer of Fig. 3(a) can be assigned to the vibrational signal of the cis C=C bond in the main chain. The band observed at a lower wavelength, 731 cm^{-1}, is assigned to that of the deformation mode of the cis C—H bond in the main chain, indicating the formation of typical cis-polyacetylene [21]. The bands at 1445 cm^{-1} observed in the PH2CP5-Rh and PH2CP5-W polymers are attributable to the CH_3 groups in the side chain for the cholesteryl moiety as observed in the dihydrocholesterol [22]. On the other hand, the wider band at ca. 1534 cm^{-1} with a shoulder at 1620 cm^{-1} observed in the PH2CP5-W polymer can also be assigned to the conjugated trans C=C bond in the main chain as has been reported by Shirakawa et al. [21]. The reason why

PH2CP5-Rh

a

731   1445   1618

1720

800   1200   1600   cm^{-1}

PH2CP5-W   1193   1534

b

1002   1127   1620

1285

1443

1720
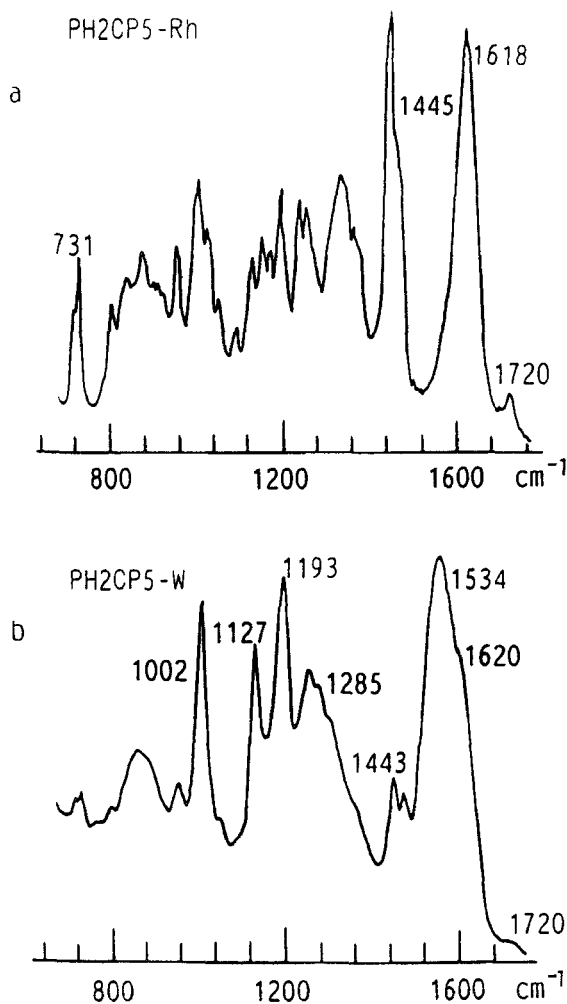
800   1200   1600   cm^{-1}

FIG. 3.   He-Ne laser Raman spectra of poly(dihydrocholesteryl pentynoate), PH2CP5
polymer. (a) Polymerized with Rh complex in triethylamine. (b) Polymerized with WCl$_6$
catalyst in dioxane.

this band has such a wide linewidth may be explained in terms of a sequence
distribution in the trans double bond formed. This is supported by the fact that a
multiplet at ca. 1285, 1193, and 1127 cm^{-1}, which can be assigned to the band of
the vibrational C—C bond coupled with the mode of the C—H deformation in the
trans sequence, is due to different chain lengths [21]. Thus the multiplet observed in
the PH2CP5-W polymer suggests that the trans sequence formed is not very long
and contains only short trans sequences although this polymer contains the cis
sequences as the minor component as can be deduced from the cis peaks at 1620 and
731 cm^{-1}, respectively.

The lengths of the double bonds produced in the PH2CP5-Rh and PH2CP5-W
polymers can be estimated. Shirakawa et al. [21] correlated the band ν_4 at around

1460–1640 cm^{-1} in the RR spectrum of the trans polyenes with the number, $N_{C=C}$, of the trans conjugated double bonds as shown in Fig. 4. Therefore, the conjugated double bond lengths in the PH2CP5-W and PH2CP5-Rh polymers were estimated as $N_{C=C} \approx 7$ and ≈ 3, respectively, assuming that the relationship can be adopted to the PH2CP5 polymers, as shown in Fig. 4. The former value, $N_{C=C} \approx 7$, is quite reasonable if the PH2CP5-W polymer is assumed to have the trans sequence as the major structure. This assignment is also supported by the fact that the PH2CP5-W polymer with an orange color showed an absorption peak at ca. 360 nm in the UV spectrum, by which the conjugation length can also be estimated as $N_{C=C} \approx 6$ if the relationship proposed by Sondheimer et al. [23] was adopted where the number of C=C bond units of the polyene is correlated with the absorption maximum in the UV spectra. Thus it is clear that conjugation lengths estimated by both laser Raman and UV spectra in the PH2PC5-W polymer are in good agreement within experimental error.

The conjugation length $N_{C=C} \approx 3$ estimated in PH2CP5-Rh clearly indicated that the PH2CP5-Rh polymer with a white color has a cis-transoid structure as we have shown for other polyacetylenes polymerized with the Rh catalyst [2, 4, 9].

Thus, the results of RR spectral studies strongly support the fact that the PH2CP5-Rh and PH2CP5-W polymers have cis-transoid and trans-transoid forms as the major structure, respectively. These observations are consistent with the Rh complex and WCl$_6$ catalysts producing polyacetylenes having the cis-transoid and trans-transoid forms as the major structures, respectively, as has been reported [1–4, 9, 24].

The sharp peak at around 1002 cm^{-1} observed in the PH2CP5-W polymer has been assigned to the deformation C—H bond in the main chain of the *trans-*
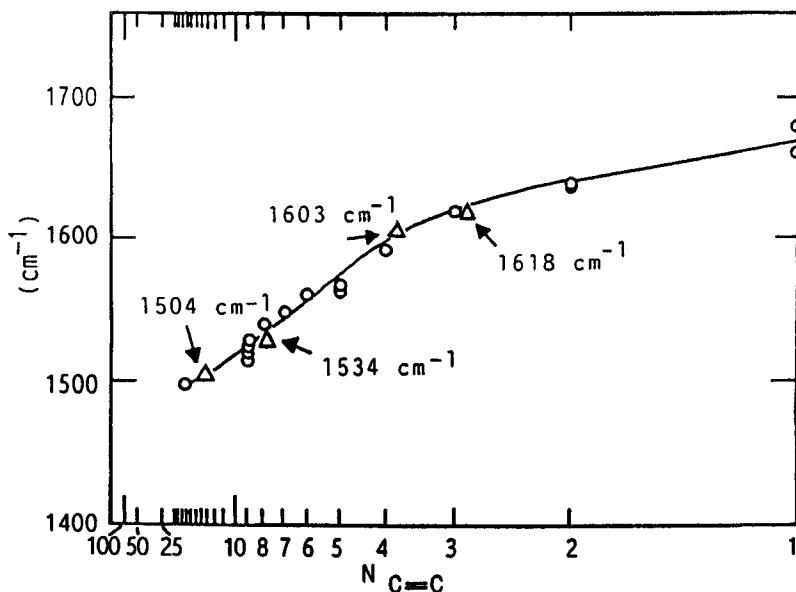

FIG. 4. Plot of laser Raman spectral band versus conjugation number, n, for polyene: (○) from Ref. 21a; (△) this work.

polyacetylene isomer as reported by Shirakawa et al. [21]. The appearance of this peak also supports the view that the WCl_6 catalyst gives a PH2CP5-W polymer having a trans sequence as a major structure. On the other hand, no intense peak at around 1000 cm^{-1} in the RR spectrum of the PH2CP5-Rh polymer was observed, suggesting that the Rh complex catalyst produced polyacetylene having a high cis-transoid content.

Figures 5(a) and 5(b) show the RR spectra of the PMBP5 polymers polymerized with the Rh complex and W catalysts, respectively. The peak at 1603 cm^{-1} observed in the PMBP5-Rh polymer was also assigned to that of the cis C=C bond of the cis-transoid polymer but not of the cis-cisoid polymer with the $N_{C=C} \approx 4$ sequence [21]. If the PMBP5-Rh polymer has the cis-cisoid structure, the cis C=C peak in the main chain should be shifted at more than 1630 cm^{-1} where no conjuga-

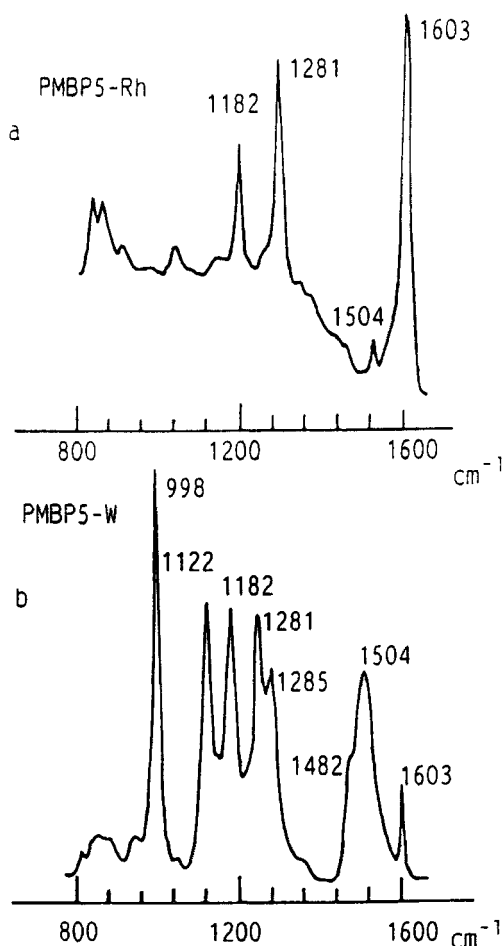FIG. 5. He-Ne laser Raman spectra of poly(p-methoxybiphenyl-4'-pentynoate), PMBCP5 polymer. (a) Polymerized with Rh complex in triethylamine. (b) Polymerized with WCl_6 catalyst in dioxane.

tion is expected, as can be deduced from Fig. 4 and Scheme 1 [22]. The very narrow linewidth of the peak observed at 1603 cm^{-1} reflects the narrow distribution of the cis component, i.e., extremely high cis-transoid content. The peak at 1504 cm^{-1} with a shoulder at 1482 cm^{-1} in the PMBP5-W polymer was assigned to the trans C=C bond [21]. The peaks observed at ca. 1281 and 1182 cm^{-1} for both polymers may be assigned to the stretching mode of the aromatic ether, and the bands at 1285 and 1122 cm^{-1} are also attributable to the C—C bond in the trans polymer with a different chain length. On the other hand, the small peak at ca. 1603 cm^{-1} may be due to a small amount of cis content. The peak observed at 998 cm^{-1} is assigned to that of the deformation C—H bond coupled with the trans C—C bond in the main chain [21]. These spectral features indicate that the PMBP5-W polymer contains the cis-transoid component as well as a fairly long trans-transoid sequence as the major component where the trans sequence can be estimated as $N_{C=C} \approx 15$–16. Thus, RR studies of the PH2CP5 and PMBP5 polymers as the aliphatic polyacetylenes revealed that the C=C bond sequence length with the cis and/or trans bonds can be estimated even when the polymer is not soluble. Studies of the thermal cis-trans isomerization and liquid crystalline properties for these pentynoate polymers are now in progress at our laboratory using DSC, polarized optical microscope, and x-ray diffraction methods.

CONCLUSION

The aliphatic acetylene ester monomers, pentynoate with a dihydrocholesteryl and 4-methoxybiphenyl group as the mesogen, and methylene as the spacer, could be stereoregularly polymerized using a Rh complex in TEA solvent to produce the polypentynoates. It was found that polyacetylene esters polymerized with the Rh catalyst have the cis-transoid form with a conjugation length of $N_{C=C} \approx 3$ while the polypentynoate polymerized with WCl$_6$ catalyst have a trans form with the conjugated sequence $N_{C=C} \approx 7$. It was also found that the main chain carbon signals, C=CH in the ^{13}C-NMR spectra of polypentynoate polymerized with the Rh complex, can be observed as strong and clear signals. Clear signals were not observed for polymers prepared using WCl$_6$ catalysts.

ACKNOWLEDGMENTS

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