π–Conjugated Columnar Polyacetylenes Prepared with Rh Complex Catalysts

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Summary: Highly stereospecific polymerization of monosubstituted acetylenes was carried out using the Rh complex, [Rh(norbornadiene)Cl]$_2$ catalysts. The resulting polyacetylenes were characterized in detail by ^{1}HNMR, ESR, laser Raman, diffuse reflective UV, and wide angle X-ray diffraction methods. The data showed that the Rh complex were the preferred catalyst to selectively yield the corresponding cis-transoid polymers even at room temperature when alcohol, triethylamine or water was used as the polymerization solvent. Additionally, the resulting cis polyacetylenes were found to have a helical form whose polymer is amorphous or composed of pseudohexagonal structures called π-conjugated columnar as self-assembly or super structure. Further compression of the amorphous cis polymers resulted in cis to trans isomerization at room temperature under vacuum, breaking rotationally the cis C=C bonds giving π-radicals called solitons as the origin of a polymer magnet. On the other hand, the π-conjugated columnar was also found to show an extremely longer wavelength absorption compared with that of the amorphous one, although the absorption maximum was shifted to a shorter wavelength when the columnar was destroyed by the compression. Therefore, the formation of the π-conjugated columnar can be considered as a new and quite useful control method concerning color of such conjugated polymers, i.e., a new concept concerning the color of conjugated polymers.

Keywords: polyacetylene; stereospecific polymers; self-assembly; catalysts; WAXS

Introduction

Scientific interest in monosubstituted polyacetylenes as π-conjugated polymer which has rapidly grown over the past years has focused recently on novel properties, in particular on photoconductivity[1-2], ferromagnetism[3-4], humidity sensor[5-6], non linear optical (NLO) materials[7-8], electroluminescence (EL) materials[9], oxygen permeability[10] and so on.

Preparation of the poly(phenylacetylene) (see **Scheme 1**) has been achieved by the use of various types of catalysts, e.g., Lutinger catalyst, Co(NO$_2$)$_2$-NaBH$_4$[11], Ziegler-Natta catalyst[12], Pt or Ni complex catalysts[13-14], and metathesis catalyst, e.g., WCl$_6$[15]. Especially

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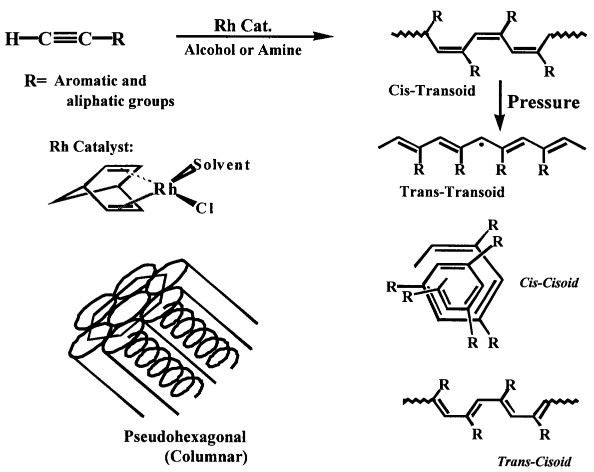
metathesis catalyst developed by Masuda and Higashimura group[15] progressed the chemistry of not only monosubstituted but also disubstituted polyacetylenes which are soluble in ordinary solvents and mainly amorphous. It is conjectured that the cis-rich polyacetylene is mainly produced by the use of $MoCl_5$ at 40°C while trans-rich polyacetylene is homogeneously produced by the WCl_6 catalyst in toluene solution[16]. Preliminary stereoregular polymerizations of phenylacetylene together with its living polymerization were first achieved using the Rh complex catalyst by Tabata's group[17-19], although the modified metathesis catalysts, Mo and W based complexes in the case of *ortho* substituted polyacetylene were used to give fairly narrow molecular weight distribution in high yields[16]. However, except for the precise control of the molecular weight and its dispersity there has been no clear and unequivocal assignment of the geometry of the resulting polymers with respect to the C=C bond in the main chain of the polymer (see **Scheme 1**), including selective formation of cis and/or trans monosubstituted polyacetylenes (**i**), copolymerization (**ii**), cis-to-trans isomerization (**iii**) at room temperature (**iv**), generation of conjugated π-radicals as solitons through the rotational scission of the cis C=C bond, and the role of the radicals to the conductivity and/or magnetism of the polymer (**v**).

Scheme 1



In this report we show the important stereospecific polymerization of monosubstituted acetylenes to selectively yield the cis form (**a**), control of the secondary structure of the relevant π-conjugated polymer chain in the solid state, i.e., formation of a pseudohexagonal structure as columnar (**b**), pressure-induced cis-to-trans isomerizations (**c**), associated with generation of π-radicals through the rotational scission of the cis C=C bonds (**d**), together with detailed characterization of the resulting polymer structures using ^{1}HNMR, ESR, laser Raman, diffuse reflective UV-Vis (DRUV-Vis), and wide angle X-ray diffraction (XRD) methods. Previously, Kern (1968)[20] has showed that the so-called Wilkinson catalyst, $RhCl(PPh_3)_3$ is active for polymerization of phenylacetylene. Recently, analogs of the catalyst were extensively developed in order to selectively produce the polyphenylacetylene, **Ia** with cis-transoid form even at room temperature[17-19, 21-22a,b], although one should be reminded that the complete cis isomer of nonsubstitued polyacetylene can be only generated at lower temperature, *ca.* -78 °C in the case of Ziegler-Natta catalyst.

Results and discussion

Stereospecific Polymerization of Aromatic Acetylenes

Previously we revealed[23] that the so-called Wilkinson complex such as $[Rh(L\text{-}L)Cl]_2$, (L-L=ligand) is the useful stereoregular catalyst for not only aromatic acetylenes but also aliphatic acetylenes, e.g., propiolates called acetylene esters[24-25] to selectively produce a cis-

Table 1. Various derivatives (I) of PPA. 1)

	R_1	R_2	R_3	R_4	[Lit.]
a:	H	H	H	H	12-14,17-22
b:	H	CH_3	H	H	34,46-47
c:	*t*-Bu	OH	*t*-Bu	H	30
d:	H	O_nC_{2n+1} (n= 1~14)	H	H	23,30,34
e:	H	H	H	O_nC_{2n+1} (n=1 and 2)	32-33
f:	H	H	H	CF_3	41
g:	H	$OCHCH\text{-}CH(CH_3)_2$	H	H	27
h:	H	$\mathrm{NH}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{C}_n\mathrm{H}_{2n+1}$ (n=1 , 3, 5, 7)	H	H	This work
i:	H	$N(CH_3)_2$	H	H	28
j:	H	NO_2	H	H	29
k:	H	$-\overset{\mathrm{O}\bullet}{\overset{\vert}{\mathrm{N}}}-t\text{-Bu}$	H	H	38
l:	*t*-Bu	$-O\bullet$	*t*-Bu	H	30
m:	H	halogen	H	H	This work

1)

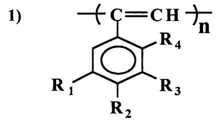
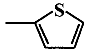
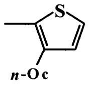
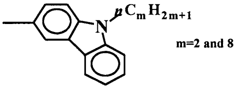
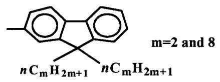
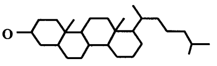
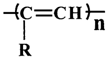


Table 2. Polyacetylenes (II) having various side chains. 1)

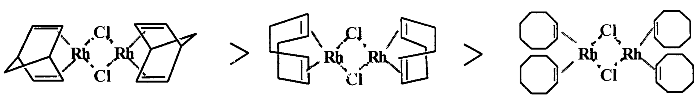
	R	[Lit.]
a:		39a
b:		39b
c:		40
d:		31
e:	$-COO\ nC_mH_{2m+1}$ (m=1~18)	24,48,52
f:	$-CH_2CH_2COO-$ 	42

1) : 

$-\!\!(\underset{R}{C}=CH)_n\!\!-$

transoid form when alcohol or amine was used under quite mild conditions (see **Tables 1, 2, 3, and 4**). We also showed that the catalytic activity in the [Rh(L-L)Cl]2 complex is shown in **Scheme 2**. This shows that the NBD ligand is strongly coordinated to the Rh atom during the polymerization without replacement of the ligand with a donor molecule[23]. We also found that the molecular weight dispersity was not narrow but approximately Mn/Mw= 2-4.

Scheme 2



[Rh(NBD)Cl]$_2$ NBD:norbornadiene

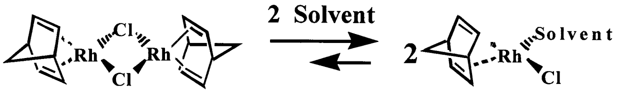
[Rh(COD)Cl]$_2$ COD:cyclooctadiene

[Rh(bis-COT)Cl]$_2$ COT: cyclooctene

Solvent Effect

Previously, we reported that an important feature of the stereospecific polymerization using the Rh complex catalyst is that alcohols[18a] or water[26-27] as an aprotic solvent or a strong organic amine, e.g., triethylamine (TEA)[19,28] can be used as the polymerization solvent.

Scheme 3



(2)

These solvents were proven to promote the dissociation of the bidentate Rh complex to a monomeric species as shown in **Scheme 3**. We also established that the order of the solvent activity[18a,b,27-29] as the cocatalyst is as follows.

$N(CH_2CH_3)_3 > ROH$ (R=aliphatic group) $\fallingdotseq H_2O$

Table 3. Polymerization results of Ia and Ig monomers by $[Rh(NBD)Cl]_2$, (Rh I) and $[Rh(COD)Cl]_2$, (Rh II), and $[Rh(bis\text{-}COD)Cl]_2$, (Rh III) catalysts under various solvents.$^{a)}$

Monomer	Rh cat.	Solvent	Yield in %	Mn X10^{4b}	Mw/Mn$^{b)}$	Cis in %
Ia	(Rh I)	TEA	100	16.0	1.76	100
Ia	(Rh I)	MeOH	90	7.31	2.13	100
Ia	(Rh I)	THF	84	6.85	3.43	85
Ia	(Rh II)	TEA	92	2.47	2.16	100
Ia	(Rh II)	MeOH	66	2.47	2.50	100
Ia	(Rh III)	MeOH	32	2.53	2.64	100
Ig$^{c)}$	(Rh I)	EtOH$^{d)}$	96	9.90	2.66	100
Ig$^{c)}$	(Rh I)	Water$^{d)}$	70	23.1	2.23	100
Ig$^{c)}$	(Rh I)	TEA	80	7.20	2.92	100

a) Polymn. temp., 30℃.; [M] = 0.5 mol/l.; [Cat.] = 0.005 mol/l.
b) Measured with GPC using chloroform as an eluent, and polystyrene as a standard.
c) [M] = 0.20 mol/l.
d) TEA was used as the cocatalyst, [Cocat.]/[Cat.] =100.

To the best of our knowledge, such solvents have not hitherto been used even in the polymerization of ordinary vinyl monomers since the start of polymer science. This indicates that the Rh catalyst is completely different from that of metathesis catalyst, such as the WCl_6[15] or Ziegler-Natta catalyst, i.e., $AlEt_3\text{-}Ti(O\textit{n}\text{-}Bu)_4$[12], which are easily deactivated by such aprotic solvents because of strong Lewis acid. This chemical property can be effectively applied in the polymerization of monosubstituted acetylenes, because even acetylene monomers, those bearing hydroxy[30], N,N'-dimethylamino[28], amide[31], alkoxy[23,32,34-36], nitro[29], hydroxyl[37], nitroxide[38], thiophens[39], and carbazole[40] groups can be polymerized under quite mild condition. This also clearly means that a new and useful stereospecific polymerization catalyst for various monosubstituted acetylenes was born to generate useful advanced materials (see **Tables 1** and **2**).

Table 4. Polymerization results of poly(phenylacetylene), Ia and poly(*p*-methylphenylacetylene), Ib initiated with $[Rh(NBD)Cl]_2$ catalyst in various solvents.a)

Monomer	Solvent	Cat. conc. mM	Yield %	Mw $x10^4$	Color	Crystallinity
Ia	EtOH	5.00	81	30.0	Yellow	*ca.* 10
Ia	Toluene	5.00	100	-[c]	Red[d]	*ca.* 60
Ib	EtOH	5.00	54	14.0b	Yellow	*ca.* 3
Ib	Toluene	5.00	54	-[c]	Red[d]	*ca.* 53

[a] Polymn. Time, 20h; Polymn. temp., 30℃; [M] = 0.7 M.

[b] THF soluble part.

[c] Insoluble in ordinary solvents.

[d] The yellow-colored polymers of **Ia** and **Ib** were immersed in toluene at room temperature for 0.5hr.

Structural Differences of Polymers Prepared with Rh Complex and Metathesis Catalyst

^{1}HNMR

Figure 1 shows the ^{1}HNMR spectrum of poly((*p*-3-methylbutyl)phenylacetylene), (**Ig** in **Table 1**) prepared with the Rh complex catalyst and observed in chloroform-d_1 ($CDCl_3$) at room temperature[27]. It is clear that the spectrum is composed of extremely sharp lines,

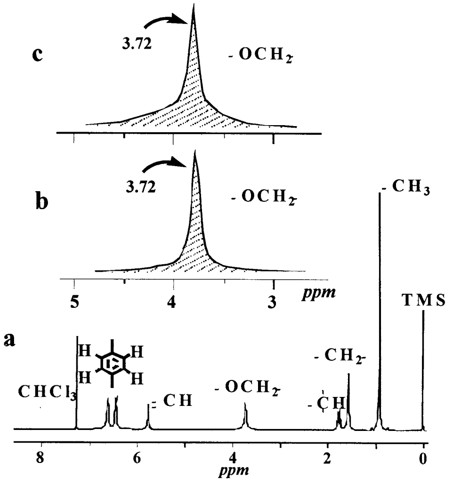


Fig. 1 ^{1}H NMR spectra of poly((*p*-3-methylbutyl)phenylacetylene))s, **Ig** (see **Scheme 2**) prepared with $[Rh(NBD)Cl]_2$ in the presence of triethylamine. (a) full scale spectrum of **Ig**, (b) expanded peak of $-OCH_2-$ protons before compression, and (c) expanded peak of $-OCH_2-$ protons after compression at $100 kg/cm^2$ under vacuum at room temperature.

suggesting highly stereospecific polymerization, i.e., selective formation of the cis-transoid isomer even if the molecular weight is very large, i.e., more than Mn = $5x10^5$.

Figure 2 shows the typical ^{1}HNMR spectrum of poly(2-octylthienylacetylene), **IIb**[39] observed at room temperature using $CDCl_3$ solution. This spectrum is composed of fairly broadened lines, although this polymer was also prepared with the same Rh complex catalyst using a mixed solvent: $CHCl_3$/TEA=100/1 (v/v) and observed in $CDCl_3$ solution at room temperature. However, in this case the cis ratio was estimated as ca. 70%, whose value was deduced with the aid of computer simulation (see **Figure 2**). This indicates that even if TEA as the cosolvent was used as the polymerization solvent no more the cis isomer was quantitatively obtained but the ratio is decreased to a large extent if a thiophene moiety is included in the monomer.

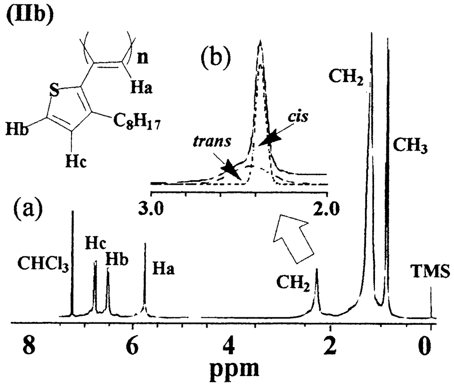


Fig. 2 ^{1}H NMR spectra of poly((2-*n*-octylthienyl)acetylene))s, **IIb** (see **Table 2**) prepared with $[Rh(NBD)Cl]_2$ in the presence of a mixed solvent: TEA/THF=1/100(v/v). (a) full scale spectrum of **IIb**, (b) expanded peak of the $-OCH_2-$ protons region in the side chain.

Figure 3 shows the ^{1}HNMR spectra of poly((*o*-trifluoromethyl)phenylacetylene), **If** which were prepared with not only the Rh complex but also the metathesis catalyst, $MoCl_5$, and observed in $CDCl_3$ solvent at room temperature[41]. It should be noted that in the case of the metathesis catalyst the spectral assignment is almost impossible unlike the case of the Rh complex catalyst as shown in **Figures 3a** and **b**. **Figure 4** shows the ^{19}FNMR spectra observed in order to deduce the possible geometrical structures [41]. The observed spectra were deconvoluted to determine, cis, trans, and boundary components connecting both isomers, together with random trans components like irregular bonds such as head-to-head

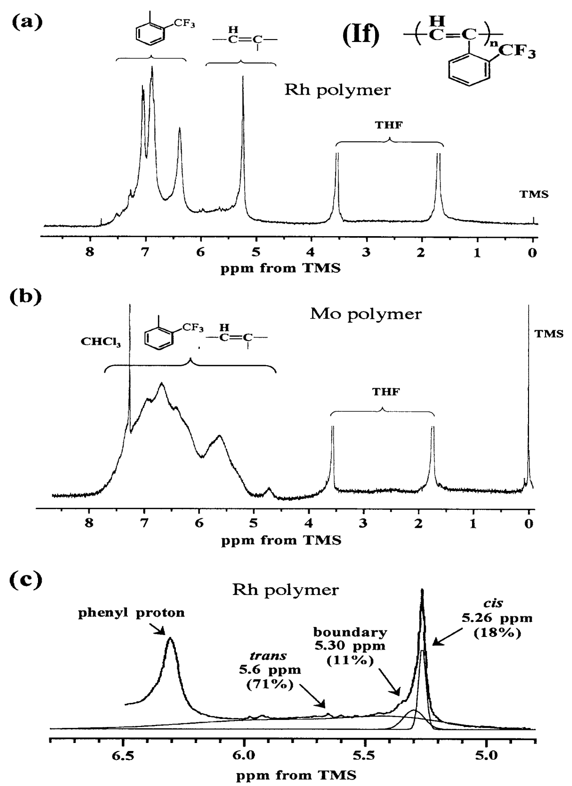


Fig. 3 ^1H NMR spectra of P((*o*-trifluoromethyl)phenylacetylene)), **If** polymers observed in THF solutions which contain a small amount of chloroform-d, 99.8 atom % with 1% v/v TMS at room temperature: (a) $[Rh(NBD)Cl]_2$ catalyst; (b) $MoOCl_4$-*n*-Bu_4Sn-EtOH catalyst; (c) expanded spectrum for $[Rh(NBD)Cl]_2$ catalyst.

and/or tail-to-tail using a computer simulation method. Thus, the data showed that the polymer (=Mo polymer) prepared with the $MoCl_5$ catalyst contains a large amount of the irregular structure as the random trans structure, i.e., head-to-head and/or tail-to-tail structures called ***disordered trans sequences***[41] together with boundary components **(see Figure 5b**). On the other hand, the latter polymer (=Rh polymer) prepared with the Rh catalyst is inversely composed of regular and repeated head-to-tail structure called ***ordered cia amd trans sequences***[41] together with the boundary components (see **Figure 5a**). It seems, therefore, that the Rh polymer is very important as a new advanced material because there is no defect in terms of the cis-trans geometrical structure.

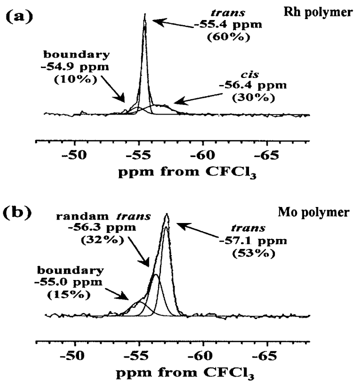


Fig. 4 ^{19}F NMR spectra of **If** polymers observed in THF-d_8 including a small amount of C_6F_6 as the internal standards at room temperature: (a) $[Rh(NBD)Cl]_2$ catalyst; (b) $MoOCl_4$-*n*-Bu_4Sn-EtOH catalyst.

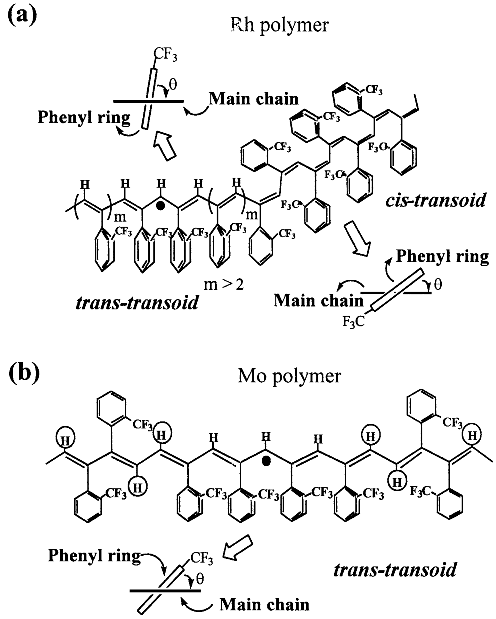


Fig. 5 Proposed conformations of **If** polymers prepared with (a) $[Rh(NBD)Cl]_2$ catalyst; (b) $MoOCl_4$-*n*-Bu_4Sn-EtOH catalyst.

Raman Study

Figure 6a shows the resonance Raman (RR) spectra of poly(dihydrocholesteryl- pentynoate)s, **IIf** prepared with the Rh complex catalyst uisng triethylamine[42]. It is clear that in the case of the Rh polymer a large peak at *ca.* 1618cm^{-1} is assigned to that of the cis main chain C=C bond, although a peak due to the carbonyl moiety in the ester group is quite small[43]. The large peak at 1445cm^{-1} may be assigned to the CH_3 or CH_2 groups which is characteristic for the aliphatic cis polyacetylenes[42a]. The peak at 731cm^{-1} was ascribed to that of the C-H bond in the cis main chain. On the other hand, **Figure 6b** shows the RR spectrum of **IIf** prepared with the so-called metathesis catalyst: WCl_6 at 40°C in dioxane[42a]. A peak at 1534cm^{-1} with a shoulder at ca. 1620cm^{-1} was assigned to that of the trans C=C bonds, and the shoulder at ca. 1620cm^{-1} can be ascribed to that of the remaining cis C=C bonds in the polymer. The peak at 1443cm^{-1} may also be due to CH_3 or CH_2 groups. The several peaks observed at 1400cm^{-1}~1000cm^{-1} may reflect the resulting ***disordered trans sequences*** as mentioned above[41-42]. The peak intensity at 731cm^{-1} due to the C-H in the cis isomer was decreased. This also means that the cis ratio is low in the W polymer compared with that of the Rh polymer. This is supported by the fact that the similar multiplet was also observed in the spectrum of the poly(*p*-chlorophenylacetylene), (**Im, R_2=Cl**) which was topochemically obtained by γ-ray irradiation of the monomer in the solid state[44].

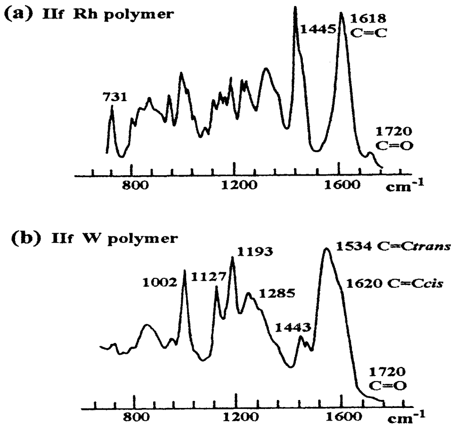


Fig. 6 Laser raman spectra of poly(dihydrocholesterylpentynoate), **IIf** polymer. (a) polymerized with the Rh complex catalyst in TEA. (b) Polymerized with WCl_6 catalyst in dioxane.

Estimation of π-Conjugation Length

Previously, we showed[33-36] that the band ν_4 at around 1460~1640cm^{-1} in the RR spectra of the trans polyenes was correlated with the number, $n_{C=C}$, of the trans conjugated C=C bonds. Therefore, the conjugated *trans* length can be estimated in the cases of **IIf** prepared with the Rh complex catalyst and the W catalyst, because the conjugation between the main-chain C=C bond and the ester group is completely decoupled by the ethylene, $-CH_2CH_2-$ moiety[42a]. Further, the two double C=C bonds in the *cis*-transoid form is *trans*-configurated to each other. On the other hand, in the cases of the trans-cisoid or cis-cisoid forms the configuration of the two C=C bonds is *cis*-configurated to each other as shown in **Scheme 1**, where such conjugation between the cis C-C bonds is not expected, if the dihedral angle between the double bonds is nearly zero degree[32,41]. Therefore, in the cases of the *trans-cisoid* and *cis-cisoid* polymers the estimation of the conjugation length is not allowed using the above relation. The trans conjugation length in the Rh polymer (**IIf**) was estimated as n=ca. 3 for 1618cm^{-1} using **Figure** 7.[42a] On the other hand, the trans conjugation length in the W polymer was also estimated as n = *ca.* 8[42a]. Thus, the geometrical configuration with respect to monosubstituted polyacetylenes can unequivocally be determined using the RR spectra. This assignment is extremely important because the possible four isomers (see **Scheme 1**)

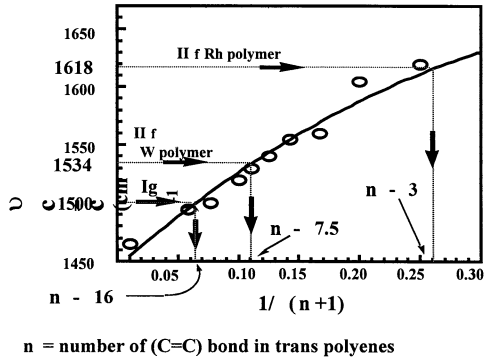


Fig. 7 Dependence of the trans conjugation length, (C=C)n, on the Raman peak of the red polymer of **Ig** polymer (**see Tables 1** and **2**) prepared with $[Rh(NBD)Cl]_2$ in the presence of triethylamine.

have not been unequivocally determined using a reliable and convenient spectroscopic method which is essential for development of new advanced materials.

Pressure–Induced cis-to-trans Isomerization

In our previous reports[29,32-36] we have shown that cis-to-trans isomerization of poly(phenylacetylene)s bearing *o*-alkoxy and *p*-alkoxy, and *p*-nitro groups as the side chain in the phenyl ring, can be induced by compression at *ca.* 100~200 kg/cm^2 under reduced pressure, ca. 10^{-2} Torr even at room temperature, when these polymers are stereoregularly prepared using a Rh complex catalyst in the presence of TEA or alcohol as the polymerization solvent.

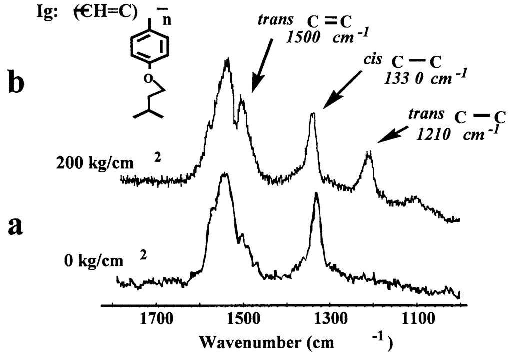


Fig. 8 Laser Raman spectra of **Ig** polymer (see **Table 1**) observed at room temperature. (a) before and (b) after compression at 200kg/cm^2 under vacuum at room temperature.

Figure 8 shows the laser Raman spectra of the red-colored polymer, **Ig**, which was prepared with the Rh catalyst using TEA solvent (see **Tables 1, 2,** and **3**) and compressed at 200kg/cm^2 under reduced pressure. It is clear that, after compression, new peaks at 1210 cm^{-1} and 1500 cm^{-1} appeared and the peak intensity at 960 cm^{-1} is decreased by the compression, though the peak at 960 cm^{-1} is not shown in **Figure 8**.

The two peaks at 1500cm^{-1} and at 1210 cm^{-1} are assigned to those of the C=C bond and C-C bond vibrations in the resulting trans form, respectively[43-44]. The peak at 1330 cm^{-1} is assigned to that of the C-C bond in the cis form which may be also superposed with that of the bond connecting the main chain with the side chain[43-44]. The conjugation length was estimated to be n≈16 for 1500 cm^{-1} as shown in **Figure** 7. Thus, it is suggested that compression of the red polymer has cis-transoid form, which undergoes cis-to-trans isomerization even at room temperature in order to create such a new trans π–conjugated sequences.

We also found that the pristine yellow **Ig** polymer showed almost the same Raman spectrum as that of the red polymer shown in **Figure 8a**. This strongly indicates that the yellow as well as the red-colored polymers have also the same cis-transoid form, suggesting a difference of the secondary structure.

Diffuse Reflective UV-Vis

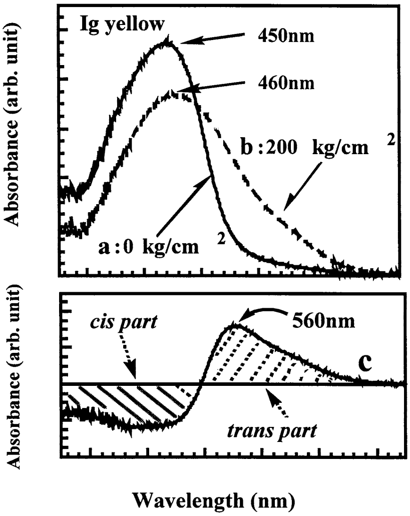


Fig. 9 Diffuse reflective UV-Vis spectra of the yellow polymer of **Ig** polymer (**see Tables 1** and **3**) observed at room temperature. (a) before and (b) after compression at 200kg/cm^2 under vacuum at room temperature, and (c) the subtraction spectrum.

Figure 9 shows the diffuse reflective UV-Vis (DRUV-Vis) spectra observed before and after compression of **Ig** with a yellow color under reduced pressure, ca. 10^{-1} Torr (see **Table 1**) at room temperature[27]. The yellow-colored polymer showed an absorption maximum, 450nm. We found that the absorption maximum in the pristine yellow polymer was shifted to a higher wavelength side when compressed, i.e., from λmax=450nm to λmax=460nm and the absorption intensity decreased. The difference spectrum obtained by subtraction of the absorption spectra observed before and after compression at room temperature is shown in

Figure 9c where a new absorption band is observed at higher wavelength, i.e., 560nm. The band observed at 560nm can be attributed to the *trans* conjugated sequences. Length of the conjugated *trans* sequences generated by the compression of the yellow polymer was also estimated, assuming that the trans conjugation length, (C=C)n, is related with the DRUV-Vis peak of the yellow **Ig** polymer as shown in **Figure 7** and **Table 5** [27].

Table 5. Absorption maxima and π–conjugation lengths, (C=C)n created by the compression of Ig polymers at room temperature.[a]

No.	Abs. max. (nm) before		Abs. max. (nm) of trans form	N in trans $(C=C)_n$	Color
1	450	460	560	29	Yellow
3	490	450	-	-	Red

[a] Polymers were compressed under vacuum at ca. 10^{-2} Torr for 10 min.

The *trans* conjugated lengths were estimated as *ca.* n=29 as shown in **Figure 10** and the data are shown in **Table 5.**

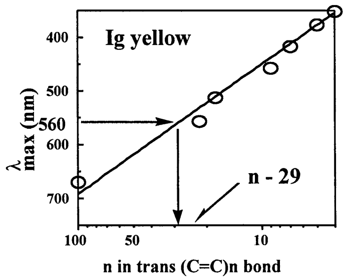


Fig. 10 Dependence of the trans conjugation length, (C=C)n, on the DRUV-Vis peak of the yellow polymer of **Ig** observed after compression at room temperature.

Figure 11 shows the DRUV-Vis spectra observed before and after compression of **Ig** having the red color under reduced pressure for 10 min. at room temperature (see **Table 1**). The red polymer showed a notably large absorption as an entire extending from ca, 300nm to ca. 840nm. However, such a long absorption tail has not been observed in other polymers which were prepared with the Rh complex catalyst. This observed chromophore may be newly explained in terms of formation of a pseudohexagonal structure called π-conjugated columnar, although this red polymer is composed of a cis-transoid form having regular head-to-tail structure as evidenced by the above Raman data. This indicates that the spectrum of the columnar polymer is attributed to that of specific π-conjugated self-assembly or self-organization which is fairly different from that of ordinary amorphous polymers, i.e., the yellow polymer, **Ig** as shown below[27]. A simple cis-transoid structure having sequences of one or two monomer units can not allow us to explain why the λmax must be observed at such

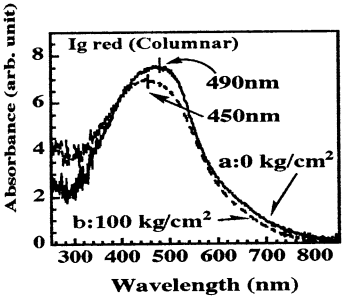


Fig. 11 Diffuse reflective UV-VIS spectra of the red polymer of **Ig** observed at room temperature. (a) before and (b) after compression at 200kg/cm^2 under vacuum at room temperature

a longer wave length region, i.e., at 490nm. Previously, we have shown that the amorphous yellow polymers, e.g., poly(*p*-methoxyphenylacetylene), (**Id**, n=1)[35] or poly(*p*-ethoxyphenylacetylene), (**Id**, n=2)[36] show the λmax at *ca.* 440nm and the absorption maximum shifted to a *longer wavelength, i.e., ca. 500~630 nm* by compression to produce the planar π-conjugated trans sequences, associated with a small peak due to that of *para* alkoxy styrene moiety[45]. On the other hand, in this experiment we also found that compression of **Ig** bearing the red color resulted in a large blue shift of the absorption maximum from 490nm to 450nm, though a shoulder appears at a shorter wavelength region of less than 300nm. Thus, compressions of the yellow and red polymers generate completely reverse phenomena regarding the shift of the absorption maximum, although the ^{1}HNMR spectra of the red and yellow polymer are completely the same in the $CDCl_3$ solution. Therefore, the observed large blue shift for the red polymer may be explained by destruction of the π-conjugated columnar as π-conjugated self-assembly, i.e., a specific aggregation of many polymer molecules in order to generate the trans π-conjugated sequences[27]. A small shoulder peak at less than 300nm is also ascribed to that of the *para*-3-methoxybutyl styrene moiety[45] in the resulting trans form as reported as before[45]. Appearance of this small peak also suggests that the *para*-3-

methylbutoxystyrene moiety plane is decoupled from the plane of the resulting trans zigzag conjugation sequences created by compression. This explanation will be strongly supported by the ESR parameters, g values observed before and after compression of the red polymer as mentioned below.

Formation of Columnar Polymer

The polymers, **Ia** and **Ib** were obtained as fine yellow powders when TEA or ethanol, EtOH was used as the polymerization solvent. On the other hand, orange colored polymers were also obtained when cyclohexanol, c-HexOH was employed. Further red colored polymers were obtained when the yellow colored polymers were immersed in toluene. We reported[46-47] that the yellow-colored polymers can be changed to the red-colored polymers by treatment with toluene (**see Ia in Table 4**). These red-colored polymers of **Ia** and **Ib** were actually insoluble in ordinary solvents such as tetrahydrofuran (THF), acetone, chloroform, and benzene unlike of **Ig**. Therefore, wide angle X-ray diffraction (XRD) patterns were observed to determine whether their polymers are amorphous or not. **Figure 12** shows the XRD patterns of **Ib** observed before and after treatment with toluene. The yellow polymer showed peaks at d=11.6Å and 4.7Å and the red colored polymer showed d=14.24Å, 7.12Å, 5.38Å, 4.75Å, 3.95Å, and 3.56Å. The latter red polymer peaks were indexed, assuming that the polymer is composed of a pseudohexagonal structure called ***columnar***[24,48-49] as molecular self-assembly or super structure where helical main-chains with cis-transoid form are packed, although the peak at ca. 4.75Å is due to amorphous halos. The indexed parameters are shown together with the columnar diameter estimated from the (100) reflection peak (see **Table 6** and **Figure 12c**). The crystalline size was also calculated as 124.4Å and 147.3Å before and after toluene treatment using the half width of the (100) reflection combined with Scherrer's equation[50]. The XRD patterns of **Ia** observed before and after the toluene treatment were nearly the same as that of **Ib**. This also indicates that **Ia** similarly forms such columnar polymers[24,27,32-36], although the columnar diameter is smaller than that of **Ib**, about 2.56 Å.

Interestingly, the peak observed at d= 3.56Å may be assigned to the helical pitch width due to the helical main-chain[48]. It is noteworthy that even the pristine yellow (**Ib**) polymer contains a small hexagonal component, i.e., *ca.* 2.5 % in the amorphous phase when ethanol was used in the polymerization, and that this content was greatly increased to *ca.* 52.5 % when the yellow polymer was immersed in toluene at room temperature. We also examined the wide angle XRD patterns observed before and after compression of the red polymer, **Ig** which was prepared using TEA solvent (see **Figure 12**)[27]. The peaks observed at 17.1Å, ~9.4Å, ~8.6Å, 6.5Å, and 4.5Å were analyzed, also assuming formation of a pseudohexagonal structure, i.e., columnar, though the (110) and (200) peaks were not clearly separated[27]. Those peaks were also attributed to the reflections of (100), (110), (200), (120), and amorphous halo, respectively. We found that the compression of the red polymer decreased the intensity of the peak at (100) reflection to a great extent. This indicates that the columnar content is decreased by the compression to make the polymer more amorphous. The columnar contents of the pristine red polymer and compressed polymer were estimated as *ca.* 53% and 34%, respectively[27]. The content of the columnar of the yellow polymer (**Ig** in **Table 1**) was also estimated as *ca.* 38%. However, the content was not found to be decreased by the compression unlike the case of the red-colored polymer.

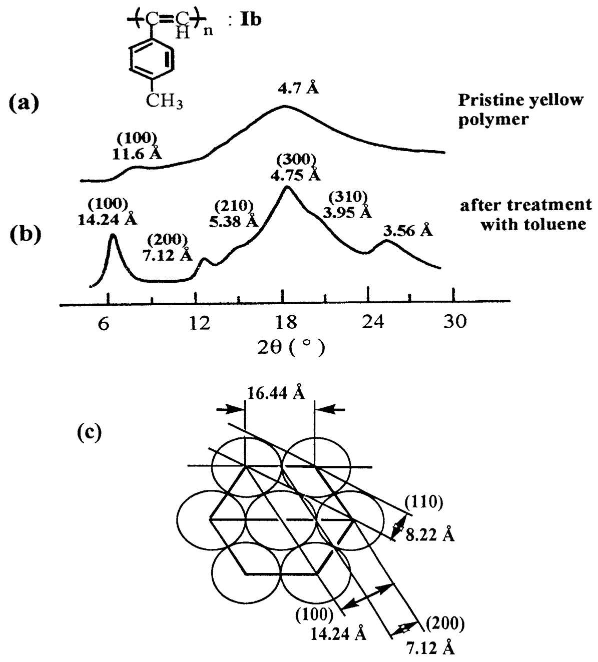


Fig. 12 X-ray diffraction patterns of **Ib** polymers observed at room temperature using Cu$K\alpha$ radiation, together with assigned indeces: (a) yellow polymer and (b) red polymer. The insert figure (c) is a pseudohexagonal structure generated by toluene treatment.

It is clearly concluded, therefore, that the columnar content of substituted polyacetylenes prepared with the Rh complex catalyst is correlated with the color, i.e., λmax (see **Figures 9** and **11**). In other word, formation of such a columnar is a preferred method to shift the original absorption of the cis polymer to longer wave length compared with that of the amorphous polymer without redesigning the polymer structure, although the crystallinity of the columnar is related with the degree of aggregation states called π–conjugated self-assembly as evidenced by the data shown above.

Table 6. Intensities and Bragg distances (Å) calculated and observed in the X-ray powder diffraction spectra and crystallite sizes (Å) calculated from (100) reflection peaks of Ib polymer synthesized with $[Rh(NBD)Cl]_2$ in triethylamine before (A) and after (B) toluene treatment.

		(A)					(B)		
hkl	d*calc.*	d*obs.*	I*obs*[a].	Size	*hkl*	d*calc.*	d*obs.*	I*obs*[a].	Size
(100)	11.62	11.6	W	124.4	(100)	14.24	14.20	VS	147.3
(110)	6.71	-	VW		(110)	8.22	-	VW	
(200)	5.81	-	VW		(200)	7.12	7.12	S	
(210)	4.39	-	VW		(210)	5.38	5.38	W	
(300)	3.87	-	VW		(300)	4.75	4.75	W	

[a]VW, Very weak; W, Weak; S, Strong; VS, Very strong.

Stable Conformations

The most energetically stable configurations of **Ia** and **Ib** were deduced using the so-called *semi-empirical quantum chemical calculation method*, AM1, where 20 monomers were used for the computer simulation[51]. **Figure 13** shows the calculated stable conformation for **Ib**.

The data showed that in the case of **Ia** and **Ib** the cis-transoid isomer takes a helical structure, approximately 8/3 helix as the most energetically stable conformation. The calculation gave rise to *ca.* 14.65Å as the diameter of the helix chain. This diameter was nearly the same as 14.65Å obtained by the XRD method. In the case of **Ia** the calculated diameter was around 12.6Å which was also very near the observed diameter, 13.34Å (see **Figure 13**).

Recently, we found that *n*-alkyl propiolate, **IIc** called acetylene ester can be also stereoregularly polymerized using the $[Rh(NBD)Cl]_2$ catalyst and the resulting polymers are not oxidized in air at all, even after more than two years and the **IIc** polymers produce also columnar which can be used as an oxygen-permeable membrane[48,52]. Therefore, this finding clearly indicates that *tri*-methylsilyl moieties as the side chains of polyacetylene are not needed for an oxygen enriched polymer unlike the case of the Masuda group[10,53].

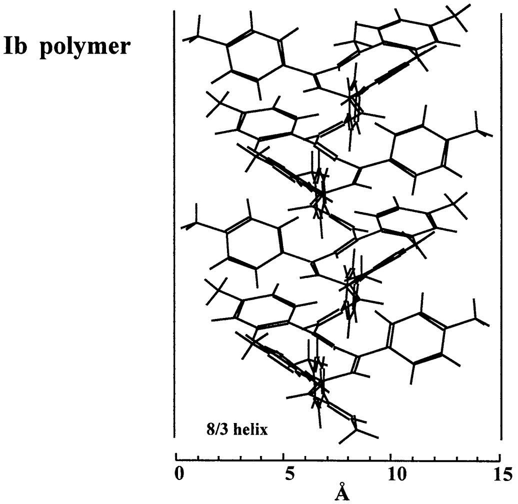


Fig. 13 Proposed helical conformation of **Ib** polymer obtained using **AM1** method.

ESR Spectra

Previously, we have shown[24,48] that the g value of not only aromatic but also aliphatic polyacetylenes such as poly(alkyl)propiolates called polyacetylene esters can be used to deduce the exact geometrical conformations, i.e., cis form or trans form, when one hetero atom such O, N, or halogen is substituted within the side chain of the polyacetylene molecules. Such a hetero atom has a relatively large spin orbit coupling constant, δ[54-55] compared with the carbon, and the hetero atom can make the observed g value shift to lower magnetic field, especially in the cis form, though such a shift in the case of the trans form is extremely small due to decoupling of the magnetic interaction between the side chain and the planar trans main-chain. This indicates that the side chain and planar trans-conjugation plane is nearly perpendicular where there is no strong magnetic interaction between the hetero atom in the side chain and the unpaired electrons. The ESR spectra were observed to determine the geometrical structure of the red polymers obtained before and after compression under vacuum for 10 min (see Figure 14)[27]. The observed parameters are shown in Table 7. It is clear that compression of the pristine red polymer decreased the g value from 2.0039 to 2.0034 and line width, ΔH*msl* from 9.8Gauss to 9.1Gauss together with a large increase of the spin concentration from $1.1x10^{16}$ spins/gram to $7.3x10^{16}$ spins/gram, strongly supporting the compression-induced isomerization from cis form to trans form[27]. The compression of the polymer under reduced pressure can break the cis C=C double bonds to produce two radical

Table 7. ESR parameters observed before and after compression of poly(3MBOPA) prepared in the presence of TEA.

Pressure (kg/cm^2)	g-Value	ΔH / (Gauss) Room temp.	ΔH / (Gauss) 77K	Spin (g) $x10^{16}$
0	2.0039	9.8	10.4	1.1
100	2.0034	9.1	11.9	7.3

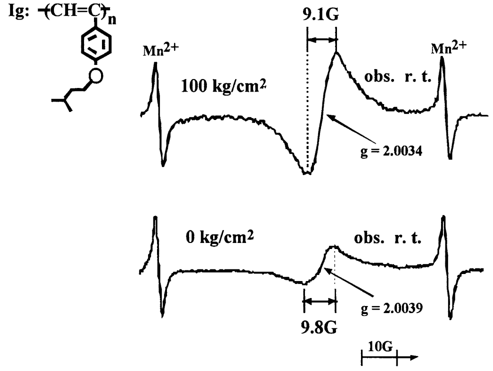


Fig. 14 ESR spectra of **Ig** polymer. (a) before and (b) after compression at 100kg/cm^2 under vacuum at room temperature. Mn^{2+} shown in this Figure is used as a standard signal of magnetic field.

spins as biradicals, and the resulting spins can stabilize in the resulting planar trans sequences as mobile unpaired electrons called solitons[56-59] which should show motional narrowing effects in the line width, i.e., the change in the line width reversibly depends on temperature change, e.g., 9.1G at room temperature and 11.9 G at 77K just as shown in **Table 7**. Thus, these data clearly indicate that the pristine polymer can be assigned to that of the cis polymer as proven by not only Raman data but also DRUV-Vis data, although the red polymer as well as the yellow polymer with a cis form can be isomerized by the compression to the trans form polymer.

Origin of Color of π-Conjugated Polymer

Thus, the results on the Raman and DRUV-Vis observed before and after compression clearly agree with those of the ESR data without any inconsistency. The red color of **Ig** is neither simply explained in terms of chromophore of the trans structure nor the cis-transoid structure as the primary structure such as repeated double-single units where the side chain moiety partly cooperated with the π-conjugated main chain as previously reported by us[27]. Therefore, it is concluded that a new chromophore as the entire peak bearing λmax at 490nm is attributed to that of a pseudohexagonal structure called columnar as π–conjugated self-assembly or self-organization. This assembly may reflect the aggregation of π-conjugated polymers which are similar to that of the so-called *J* aggregation of LB molecules[60-61]. This is a new and important concept because preparation of π–conjugated polymers having columnar structure is a new method to control the color of the conjugated polymer which can be used as new and promising advanced materials such as NLO[62] or EL materials[63] in the solid state.

Conclusion

Stereoregular polymerization of monosubstituted acetylene was successfully performed using the $[Rh(NBD)Cl]_2$ catalyst in the presence of various solvents at around room temperature to selectively produce the corresponding cis-transoid polymer which can make a pseudohexagonal structure called columnar as self-assembly in high yields. The poly(phenylacetylene) derivatives obtained before and after not only solvent treatment but also compression under vacuum were characterized in detail using ^{1}H NMR, Raman, ESR, diffuse reflective UV-Vis, and X-ray diffraction methods. Consequently, the pristine polymer prepared using triethylamine manifested that the red color arises from that of the columnar as the π–conjugated self-assembly whose content can be also decreased with compression associated with a large blue shift of the absorption maximum in the UV-Vis spectrum of the original polymer. Thus, formation and destruction of the columnar as π–conjugated self-assembly of a conjugated polymer such as **Ia** or **Ig** is a very important concept for the color design of π-conjugated polymers, i.e., absorption maximum which may be related with ionization potential, *IP* as well as the Stokes shift on LED materials. Therefore, the columnar formation becomes a new method to control the color of the conjugated polymer even in the cis form without formation of trans polymers.

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