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### Columnar Formation from Polyethynylbenzene and Poly-(*p*-Methylethynylbenzene) Polymerized Using [Rh(norbornadiene)Cl]<sub>2</sub> as a Catalyst. An X-ray and ESR Study

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## **COLUMNAR FORMATION FROM POLYETHYNYLBENZENE AND POLY- (*p*-METHYLETHYNYLBENZENE) POLYMERIZED USING [Rh(NORBORNADIENE)Cl]<sub>2</sub> AS A CATALYST. AN X-RAY AND ESR STUDY**

MASAYOSHI TABATA,\* SHIN KOBAYASHI,  
YOSHIKAZU SADAHIRO, YUJI NOZAKI,  
KAZUAKI YOKOTA, and WU YANG

Department of Molecular Chemistry  
Graduate School of Engineering  
Hokkaido University  
Sapporo 060, Japan

**Key Words:** Polyethynylbenzene; Rh complex catalyst; Stereoregular polymerization; Columnar; ESR

### **ABSTRACT**

Stereoregular polymerization of *p*-methylethynylbenzene (MEB) was successfully performed using a [Rh(norbornadiene)Cl]<sub>2</sub> catalyst in alcohol and triethylamine. Polymers which have a *cis*-*transoid* structure were selectively formed in fairly high yields. The structure and properties of the resulting polymers were compared with those of polyethynylbenzene (PEB) by means of x-ray diffraction and ESR techniques. The data showed that both pristine amorphous polymers are converted to pseudohexagonal structures called columnar when they were treated with toluene at room temperature. The line width,  $\Delta H_{msl}$  in the ESR spectrum of PMEB polymer was found to be increased from 10.5–12.5 gauss to 13.1–15.8 gauss when the solvent was changed from alcohols, e.g., ethanol or *tert*-butanol, to cyclic alcohols, e.g., cyclopentanol. The increase of the observed  $\Delta H_{msl}$  was explained in terms of magnetically inhomoge-

neous broadening arising from heterogeneous aggregations of radical spins in the columnar polymer phase.

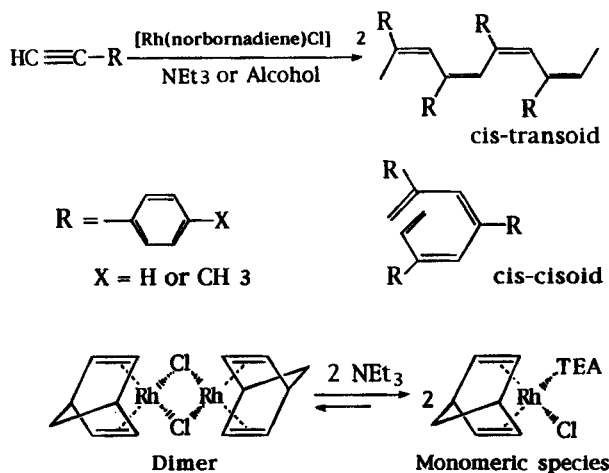
## INTRODUCTION

In previous papers [1-4] we reported that ethynylbenzene (EB) and its homologues can be stereoregularly polymerized using Rh complex such as  $[\text{Rh}(\text{norbornadiene})\text{Cl}]_2$ ,  $[\text{Rh}(\text{NBD})\text{Cl}]_2$ , in the presence of alcohol or triethylamine as the cocatalyst to give polyacetylenes which are rich in cis-transoid structures. We also showed that the Rh complex is useful for the living polymerization of *m*-chloroethynylbenzene when triethylamine is used as the polymerization solvent. The triethylamine was proposed to function, based on UV spectral data [3], by promoting the dissociation of the bidentate complex,  $[\text{Rh}(\text{norbornadiene})\text{Cl}]_2$ , into the monomeric species,  $\text{Rh}(\text{norbornadiene})\text{Cl}$ -triethylamine, as shown in Scheme 1.

Further, we also reported that the PEB polymer was insoluble in ordinary solvents, e.g., benzene, when the molecular weight, MW, exceeded around 10,000 [2]. We recently also found that polymers such as poly(*n*-alkylpropiolate) (PAPP) [5], polypentynoate (PAPN) [6], and poly(*o*-methoxyethynylbenzene) (POMEB) [7] polymerized in a stereoregular fashion in the presence of the Rh complex catalyst to give pseudohexagonal structures, which we referred to as columnar phases. These findings suggest that not only can the geometrical structure with respect to the C=C bond in the main chain but also the secondary structure be controlled to produce a hexagonal columnar structure, i.e., self-organization.

In this communication a stereoregular polymerization of EB and MEB monomers induced by the Rh complex catalyst in various solvents is reported, together with detailed characterizations of the resulting polymers using x-ray diffraction and electron spin resonance (ESR) methods.

The control of geometrical and secondary structures of polyacetylenes is important, since such structures can be correlated with physicochemical properties,



SCHEME 1.

e.g., oxygen permeability [8], ferromagnetism [9–11], and nonlinear optical (NLO) susceptibility [12, 13]. Therefore, the stereoregular polymerization of the EB and MEB monomers using the Rh complex-triethylamine or alcohol catalyst was adopted in order to precisely control the geometrical structure as not only the primary structure but also the secondary structure as a molecular assembly or self-organization in the solid state.

## EXPERIMENTAL

### Materials

Rhodium complex,  $[\text{Rh}(\text{NBD})\text{Cl}]_2$ ,  $[\text{Rh}(\text{cyclooctadiene})\text{Cl}]_2$ ,  $([\text{Rh}(\text{COD})\text{Cl}]_2)$ , and ethynylbenzene (EB) (from Aldrich) were used as received. *Para*-methylethynylbenzene (MEB) was synthesized according to the literature [2] and purified by distillation under reduced pressure (42–43°C/8 torr). The polymerization solvents, triethylamine (TEA), tetrahydrofuran (THF), and alcohol, were purified and dried according to standard methods.

### Polymerizations

Polymerization reactions were carried out at a monomer concentration of 5 mM and a temperature of 30°C for 24 hours. When a solvent such as methanol or TEA was used as a cocatalyst, the polymers precipitated as a fine yellow powder during the reaction. The resulting polymer powder was isolated on a filter, washed with excess warm methanol (100 mL), and dried under reduced pressure at approximately  $10^{-3}$  torr for 24 hours. The polymerization was stopped by addition of a large excess of methanol to the reaction solution to greatly decrease the catalytic activity of the Rh complex.

### Analyses

The molecular weights were determined by gel permeation chromatography (GPC) calibrated with a polystyrene standard and equipped with two TSK columns (G2000H8 and G5000H6, THF solvent) from TOSOH Ltd.

Electron spin resonance (ESR) spectra were recorded on a Jeol FE1XG using 100 kHz field modulation at room temperature. X-ray diffraction patterns (XRD) were measured on a Jeol JDX 8020 using a nickel-filtered  $\text{CuK}\alpha$  source at room temperature.

## RESULTS AND DISCUSSION

Stereoregular polymerization of MEB using the Rh complex and the  $[\text{Rh}(\text{COD})\text{Cl}]_2$  and  $[\text{Rh}(\text{NBD})\text{Cl}]_2$  catalysts in the presence of various solvents were performed in order to determine which catalyst had the greatest polymerization activity. These results are shown in Tables 1 and 2, along with data on the EB monomer. It is clear that  $[\text{Rh}(\text{NBD})\text{Cl}]_2$  combined with triethylamine gives rise to the highest yields for the EB monomer compared with alcohol, indicating that TEA

TABLE 1. Polymerization Results of *p*-Methylethynylbenzene (MEB) and Ethynylbenzene (EB) Initiated with [Rh(COD)Cl]<sub>2</sub> in Ethanol Solvents<sup>a</sup>

No.	Monomer	Solvent	Catalyst concentration, mM	Yield, %	MW <sup>b</sup> × 10 <sup>4</sup>	Color
1	MEB	EtOH	7.00	38.1	5.2	Yellow
2	EB	EtOH	7.00	53.7	7.6	Yellow

<sup>a</sup>Polymerization time, 20 hours; polymerization temperature, 30°C; monomer concentration, 0.7 M.

<sup>b</sup>THF-soluble part.

works as a powerful cocatalyst for this polymerization because of the dissociating reagent from the dimer Rh complex to the monomeric species as shown in Scheme 1. The resulting polymers were fine yellow powders when triethylamine or alcohols, e.g., ethanol, was used as the solvent, and orange-colored polymers were obtained when cyclic alcohols such as cyclopentanol were employed. Interestingly, the molecular weight, MW, of the PEB polymer was inversely proportional to the catalyst concentration, reaching the highest molecular weight, MW = 442.8 × 10<sup>4</sup>, at the

TABLE 2. Polymerization Results of *p*-Methylethynylbenzene (MEB) and Ethynylbenzene (EB) Initiated with [Rh(NBD)Cl]<sub>2</sub> in Various Solvents<sup>a</sup>

No.	Monomer	Solvent	Catalyst concentration, mM	Yield, %	MW × 10 <sup>4</sup>	Color
1	MEB	MeOH	7.00	48.0	5.0 <sup>b</sup>	Yellow
2	MEB	EtOH	5.00	54.0	14.0 <sup>b</sup>	Yellow
3	MEB	<i>n</i> -PrOH	7.00	60.0	25.0 <sup>b</sup>	Yellow
4	MEB	<i>t</i> -BuOH	7.00	85.0	68.0 <sup>b</sup>	Yellow
5	MEB	<i>c</i> -PenOH	7.00	67.4	4.0 <sup>b</sup>	Orange
7	MEB	<i>c</i> -HexOH	7.00	67.0	17.0 <sup>b</sup>	Orange
8	MEB	EtOH (toluene)	5.00	54.0	—	Red <sup>c</sup>
9	EB	EtOH	5.00	81.0	30.0	Yellow
10	EB	TEA	5.00	100	102.2	Yellow
11	EB	TEA	1.00	100	139.0	Yellow
12	EB	TEA	0.50	100	164.0	Yellow
13	EB	TEA	0.05	27.0	286.6 <sup>b</sup>	Yellow
14	EB	TEA	0.01	9.4	442.8 <sup>b</sup>	Yellow
15	EB	TEA (toluene)	0.05	100	—	Red <sup>c</sup>

<sup>a</sup>Polymerization time, 20 hours; polymerization temperature, 30°C; monomer concentration, 0.7 M.

<sup>b</sup>Part soluble in THF.

<sup>c</sup>Polymers of 2 and 10 were immersed in toluene at room temperature for 0.5 hour.

lowest concentration of catalyst, 0.01 mM. This suggests that the catalyst activity for the EB monomer is very high, even at such a low catalyst concentration.

Orange-colored PMEB polymers were obtained when a cyclic alcohol such as cyclopentanol was used as cocatalyst. We found that the yellow-colored polymers became red on treatment with toluene (see No. 8 in Table 2).

These yellow, orange, and red PMEB polymers were almostly insoluble in ordinary solvents such as tetrahydrofuran, acetone, chloroform, and benzene. Therefore, x-ray diffractions (XRDs) of the yellow- or red-colored polymers were performed in order to determine if they were amorphous or not. Figure 1 shows the XRD patterns of PMEB polymers observed at room temperature before and after

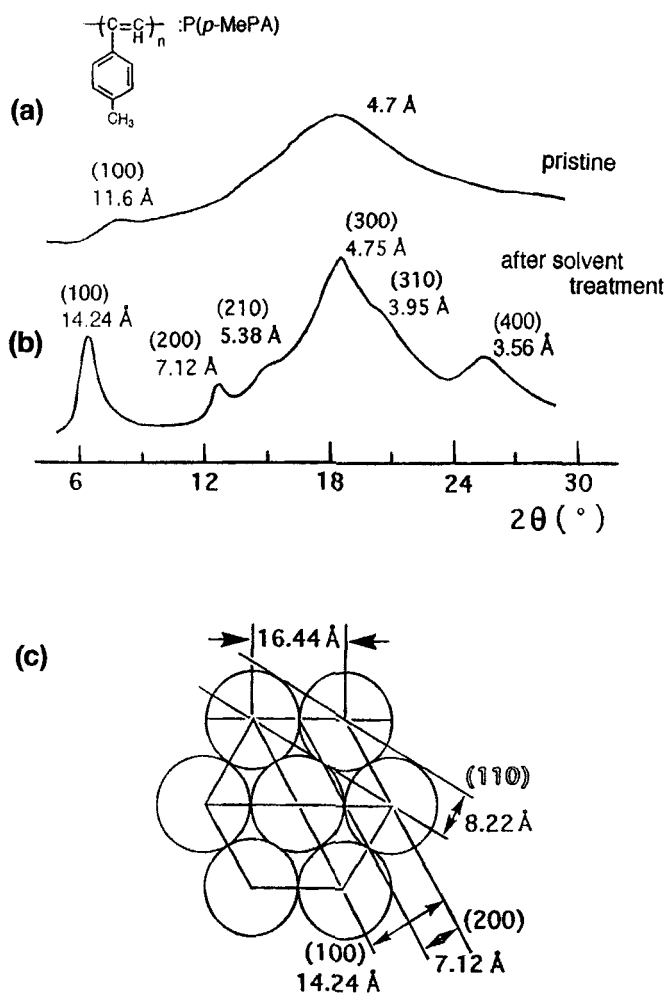


FIG. 1. X-ray diffraction patterns of PMEB polymers observed at room temperature together with assigned indices. Yellow polymer, a (No. 2 in Table 2), and red polymer, b (No. 8 in Table 2). The inset figure c is a pseudo-hexagonal structure generated by the toluene treatment.

treatment with toluene. The pristine PMEB polymer is amorphous as evidenced by the halo peak at 4.7 Å, although a small peak appeared at  $2\theta \approx 7.6^\circ$ ,  $d \approx 11.6$  Å as shown in Fig. 1(a).

After toluene treatment, however, several new peaks appeared at the higher angle side as shown in Fig. 1(b). These peaks were indexed assuming that a pseudo-hexagonal structure (columnar phase) was formed by the toluene treatment of the amorphous polymer, i.e., seven polymer chains are bundled within a unit column in each columnar tube as shown in Fig. 1(c). Therefore, the XRD pattern of PMEB observed after the treatment was analyzed as follows: the peaks at the lower angle side ( $d = 14.24$  Å) and at higher angle sides ( $d = 7.12, 5.38, 4.75, 3.95,$  and  $3.56$  Å) were assigned to the (100), (200), (210), (300), (310), and (400) reflections, respectively, based on the pseudo-hexagonal structure. Taking this assignment into account, we assigned the small peak,  $d \approx 11.6$  Å observed in the pristine yellow polymer, to the (100) reflection of the hexagonal form. It is noteworthy that even the pristine yellow PMEB polymer contains a small hexagonal component (approximately 2.5%) in the amorphous phase when ethanol is used in the polymerization, and that this content is greatly increased to approximately 52.5% when the yellow polymer is immersed in toluene at room temperature (referred to as the toluene treatment). The observed and calculated XRD parameters in the PMEB polymer are shown in Table 3.

The crystallite sizes before and after toluene treatment were calculated from the linewidth at the (100) reflection, and the results are shown in Table 3. It is interesting that the crystallite size can be changed by solvent treatment, i.e., 124.4 Å before treatment and 147.3 Å after toluene treatment. This shows that toluene induces an increase of the hexagonal crystallite size of the aromatic polyacetylenes. The diameters of the columnars of the PMEB polymers before and after toluene treatment were calculated as 13.39 and 16.44 Å, respectively, using the reflection data shown in Figs. 1(a), 1(b), and 1(c).

TABLE 3. 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 PMEB Polymers (No. 2 in Table 2, a; and No. 8 in Table 2, b)

a					b				
<i>hkl</i>	$d_{\text{calc}}$	$d_{\text{obs}}$	$I_{\text{obs}}^a$	Size	<i>hkl</i>	$d_{\text{calc}}$	$d_{\text{obs}}$	$I_{\text{obs}}$	Size
(100)	11.62	11.6	W	124.4	(100)	14.24	14.2	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)	4.78	4.75	S	
(310)	3.22		VW		(310)	3.95	3.95	W	
(400)	2.52		VW		(400)	3.56	3.56	S	

<sup>a</sup>VW, very weak; W, weak; S, strong; VS, very strong.

A similar color change together with an increase of the crystallite size were also observed for the case of PEB polymer when the yellow-colored polymer (No. 10 in Table 2) was treated with toluene. Therefore, the observed XRD patterns were also analyzed assuming the formation of a similar columnar phase. These results are shown in Fig. 2. The calculated and observed XRD parameters are shown in Table 4.

It is important to note that the  $d$  spacing of the hexagonal PMEB polymer is larger by approximately 2.56 Å than that of the PEB polymer. The difference observed in the columnar diameter may be ascribed to the molecular size difference between phenyl and *p*-methylphenyl moieties in the side chains of the polyacetylene because the molecular size difference is estimated to be approximately 2.6 Å using molecular models. This suggests that the diameter of the core molecule in the polyacetylenes is not changed as a function of the size of the side group. Thus we were able to analyze the XRD patterns of the PMEB, as well as the PEB polymer before and after toluene treatment.

It has been reported that soluble and amorphous PEB polymer (SA) can be obtained using a Ziegler-Natta catalyst, e.g.,  $\text{AlH}(i\text{-Bu})_2\text{-Fe}$  acetylacetonate together with a so-called insoluble and crystalline component (IC) [14]. The amorphous component (SA) showed a halo peak similar to that shown in Fig. 2(a). On the other hand, the XRD pattern of the crystalline part (IC) showed several peaks which almost agree with those shown in Fig. 2(b) although the (IC) component was

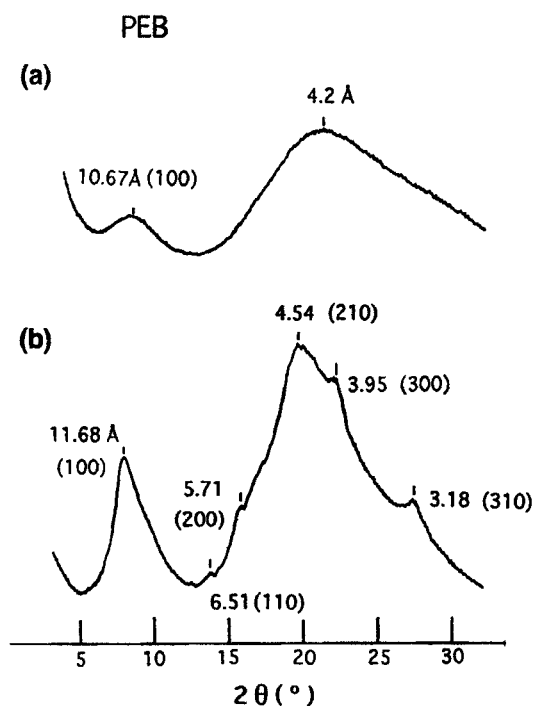


FIG. 2. X-ray diffraction patterns of PEB polymers. Yellow polymer, a (No. 9 Table 2) and red polymer, b (No. 15 in Table 2), colors.



TABLE 4. 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 PEB (No. 9 and 15 in Table 2) Synthesized with [Rh(NBD)Cl]<sub>2</sub> in Triethylamine before (a) and after (b) Toluene Treatment

a					b				
<i>hkl</i>	<i>d</i> <sub>calc</sub>	<i>d</i> <sub>obs</sub>	<i>I</i> <sub>obs</sub> <sup>a</sup>	Size	<i>hkl</i>	<i>d</i> <sub>calc</sub>	<i>d</i> <sub>obs</sub>	<i>I</i> <sub>obs</sub>	Size
(100)	10.67	10.67	W	61.3	(100)	11.68	11.68	VS	70.8
(110)	6.16	—	VW		(110)	6.74	6.51	VW	
(200)	5.34	—	VW		(200)	5.84	5.71	S	
(210)	4.03	—	VW		(210)	4.42	4.54	W	
(300)	3.56	—	VW		(300)	3.89	3.95	W	
(310)	2.96	—	VW		(310)	3.24	3.18	S	

<sup>a</sup>VW, very weak; W, weak; S, strong; VS, very strong.

assigned to that of the cis-cisoid structure with a 3/1 helix. Other Ziegler–Natta catalysts, AlEt<sub>3</sub>-rare earth naphthenates, were also used to produce PEB polymer [15] which contains both SA and IC components. However, the previous XRD patterns for the IC components in the literatures have not been identified as the hexagonal reflection.

Recently Unger proposed that columnar polymers can be classified as liquid crystals in cases in which they do not exhibit positional long-range order (PLRO) along the molecular axis [16]. Such structures have also been referred to as “rotor,” “liquid crystal,” “smectic,” “hexagonal crystal,” simply “thermotropic,” and “condis (= conformational disorder) crystals” [16].

Hexagonal polymer chains packed in a column are also conjectured to be rotated in each column where the molecular axis distance, i.e., the *c* axis, cannot be estimated because it is effectively infinite [16].

Helicoidal PEB polymers having a rigid and rodlike structure have been postulated by Ehrlich and his group [14]. They reported that a crystalline PEB polymer which was repeatedly treated with a mixture of CDCl<sub>3</sub> and CCl<sub>4</sub> displayed birefringence as a liquid crystal-like order, although the crystalline structure of the PEB has not been identified by them. Thus, it appears that the previous observations with respect to the crystallinity and helical structure of the PEB polymer agree well with those in this report.

The diameter of the column and the crystallite size may be related to properties of considerable technological importance. Some polymers bearing a hexagonal packing structure are highly permeable to gas in the glassy hexagonal state [17]. Therefore, *the formation of such columnar structures, i.e., self-organization, constitutes an important feature of polyacetylenes which are stereoregularly prepared using a Rh complex catalyst in alcohol or triethylamine.*

Figure 3 shows ESR spectra of PMEB polymers polymerized with ethanol (a) and cyclohexanol (b) solvents at 30°C (see Table 2). These studies show that an increase in the linewidth,  $\Delta H_{\text{msl}}$  (gauss) in the ESR spectra took place when the polymerization solvent was changed from a EtOH or *tert*-butanol (No. 2 or 4 in

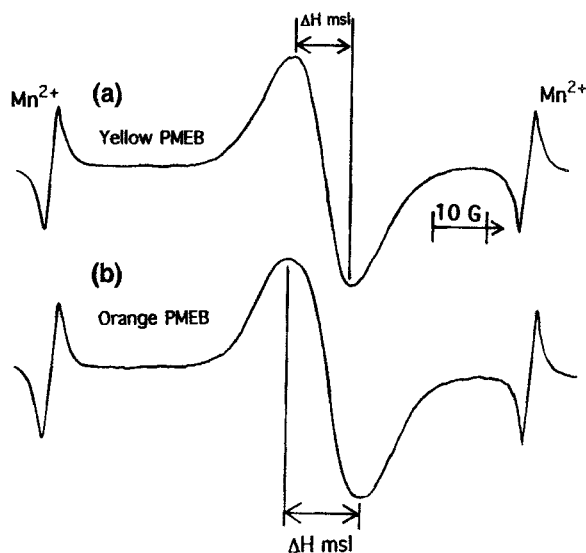


FIG. 3. ESR spectra observed in the PMEB polymers with the yellow, a (No. 2 in Table 2), and orange, b (No. 5 in Table 2).

Table 5) to a cyclic alcohol, e.g., *c*-penOH (No. 5 in Table 5), although neither the spin concentration of radicals stabilized in the main chain nor the *g*-value (2.00264) changed appreciably.

The ESR parameters for the polymers are shown in Table 5. To the best of our knowledge, such increases in linewidth,  $\Delta H_{msl}$ , have not been reported. The increase in linewidth may be interpreted in terms of magnetic interaction between radical spins stabilized in the polymer chains, i.e., inhomogeneous broadening arising from

TABLE 5. ESR Parameters and Color of PMEB Polymer Obtained Using  $[\text{Rh}(\text{NBD})\text{Cl}]_2$  as a Catalyst in the Presence of Various Solvents<sup>a</sup>

No. <sup>b</sup>	Solvent	Color	Spin concentration, spins/g	$\Delta H_{msl}$ , G
2	EtOH	Yellow	$2.7 \times 10^{16}$	10.8
3	<i>n</i> -PrOH	Yellow	$2.0 \times 10^{16}$	12.5
4	<i>t</i> -BuOH	Yellow	$1.8 \times 10^{16}$	10.5
5	<i>c</i> -PenOH	Orange	$2.1 \times 10^{16}$	15.8
6	<i>c</i> -HexOH	Orange	$1.7 \times 10^{16}$	15.5
7	Toluene <sup>c</sup>	Red	$3.0 \times 10^{16}$	13.1

<sup>a</sup>Observed at room temperature using a shielded quartz tube.

<sup>b</sup>Number in Table 2.

<sup>c</sup>The polymer of No. 2 was immersed in toluene for 0.5 hour at room temperature.

heterogeneous aggregation of inter- and/or intrapolymer radicals [18]. It is thought that such a pseudohexagonal structure is composed of the aggregated polymer chains which would statistically have radical spins (called soliton) produced by rotational scission of the C=C bond in the cis form during and/or after the polymerization [4, 19, 20]. Therefore, cyclohexanol, when used as the solvent, may induce coagulation of *cis*-polyacetylene chains, giving rise to the columnar as a self-organization. This process may involve many radical spins which are stabilized in the cis main chain as immobile unpaired electrons, as reported previously [19, 20]. This suggests that, in the hexagonal solid state, the distribution of the radical spins is not homogeneous but heterogeneous. Such magnetically inhomogeneous interactions between the spins within the polymers would be expected to increase the linewidth observed in the ESR spectra, as shown in Fig. 3(b). This interpretation is not unreasonable because the line shape observed after the treatment can be well simulated using so-called Gaussian line shape compared with that of the spectrum observed before the treatment [18]. However, alcohols such as EtOH or *t*-BuOH as solvent do not increase the linewidth where the radical spins are distributed homogeneously and/or at random due to the existence of an amorphous state, even though the hexagonal phase may be present in the amorphous polymer to a small extent as can be seen in Fig. 3(a). Such magnetically inhomogeneous radical spin interactions between inter- and/or intrapolymer chains in the hexagonal phase, i.e., columnar phase, may induce the increases of the linewidth. Thus the differences in the linewidth  $\Delta H_{msl}$  among the cases in which different solvents were used can be explained in terms of the degrees of the magnetically inhomogeneous interaction between the spins stabilized in the cis polymer phase, because the spin concentrations of each polymer were not notably increased upon toluene treatment.

A similar solvent-induced color change was found in the PEB polymer when the yellow polymer (No. 10 in Table 2) was treated with toluene to give a polymer having a red color (No. 15 in Table 2). For the latter, the linewidth in the ESR spectra was increased from approximately 12 to 14 G, suggesting a rather small magnetically inhomogeneous line broadening interaction.

It is also noteworthy that the hexagonal phase, as a secondary structure resulting from polyacetylene polymers, constitutes a useful architecture that allows bundling of not only radical polymer chains but also of nonradical polymer chains at the molecular level, i.e., on a nanoscale. The hexagonal structure generated by the treatment, however, may involve ordered polymer chains and/or disordered polymer chains with and/or without the radical spins as shown in Fig. 4. The hexagonal structure may also be composed of tie molecule chains which connect the hexagonal columnar tubes, as has been observed in the case of polyethylenes [21], as shown in Fig. 4.

The linewidth of the ESR spectra of the polymers showed no motional narrowing, even when the PMEB polymers were cooled from room temperature to 77 K, as reported in the case of polyethynynaphthalene (PENAP) [19, 20] and poly(*o*-methoxyethynylbenzene) (POMEB) polymers [7] polymerized with the Rh complex catalyst. This suggests that the radical spins generated during the polymerization and/or after the polymerization are stabilized in the *cis*-transoid form where the unpaired electrons cannot move around along the main chain because of the restricted *cis*-conjugated chain [19, 20].

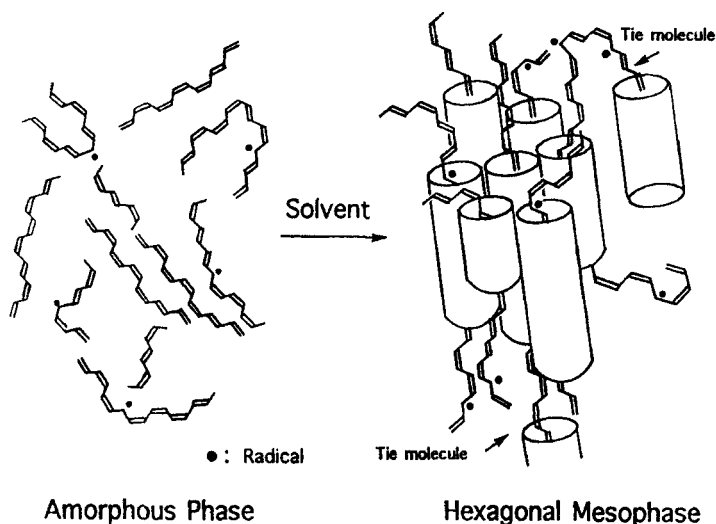


FIG. 4. Amorphous phase and pseudo-hexagonal mesophase called columnar bearing ordered and disorder polymer chains. The disordered chains may constitute polymer radical chains and tie molecules connecting other columns.

It appears that the polymer chains which are packed in the hexagonal column may be helical chains which stabilize the columnar structure. The helical structure of PEB polymer has been described by Sanford et al. [14], Simionescu et al. [22], and recently by us [5] and Yashima et al. [23] using molecular mechanics and dynamics calculations. The calculations supported the proposition that the cis-transoid structure of the PEB polymer is a helical one, as has been deduced previously. However, if the cis-transoid polymer is composed of the helicoidal structure, it will be difficult to distinguish structural differences between the cis-cisoid polymer having an approximately 3/1 helix [14] and a helicoidal cis-transoid polymer if the data regarding the *c*-axis distance along the molecular axis in both cases is not known. Unfortunately, for hexagonal polymers the *c*-axis distance cannot be determined by the XRD method due to the effectively infinite distance.

It is not unreasonable to assume that such rigid rodlike hexagonal polymers are not dissolved in ordinary solvents, as observed in this study. Therefore, insolubility of monosubstituted polyacetylene polymers, in particular solvent-treated PEB, PMEB, POMEb [7], poly(methylpropiolate) [5], poly(ethynylpyridine) [24], and poly(*p*-methoxybiphenyl pentynoate) [6], may be in part attributed to the hexagonal packing. This would prevent such polymers from being easily solvated because of their rather narrow helical pitch.

## CONCLUSIONS

Stereoregular polymerizations of ethynylbenzene (EB) and *p*-methylethynylbenzene (MEB) were achieved using  $[\text{Rh}(\text{NBD})\text{Cl}]_2$  as a catalyst in the presence of alcohol or triethylamine as a cocatalyst. The resulting polymers, obtained in high

yields, were cis-transoid in form. It was found, however, that the pristine amorphous polymers, which were yellow in color, could be transformed to the pseudo-hexagonal polymers, which were red in color, by treatment with toluene. It was also concluded that polyacetylenes, PEB, and PMEB polymers together with POMEb [7], PAPP [5], and PAPAN [6] polymers are also composed of typical hexagonal structures when produced using the Rh complex catalyst in the presence of triethylamine or cyclic alcohols. This formation of hexagonal polyacetylene polymer having a cis-transoid form is one of the most important features of polyacetylene which was prepared using a Rh complex catalyst.

It was also found that toluene treatment of the yellow PEB and PMEB resulted in an increase in the linewidth of the ESR spectra. This increase was interpreted in terms of the magnetically inhomogeneous broadening between the radical spins heterogeneously distributed in the columnar phase.

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