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Origin of Color of π-Conjugated Columnar Polymers. 1. Poly(p-3-methylbutoxy)phenylacetylene Prepared Using a [Rh(norbornadiene)Cl]$_2$ Catalyst

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ABSTRACT: Stereoregular polymerization of (p-3-methylbutoxy)phenylacetylene (p3MBPA) was successfully performed with a [Rh(NBD)Cl]$_2$ catalyst to afford poly(p-3-methylbutoxy)phenylacetylene (Pp3MBPA) having a cis-transoid form in high yields when ethanol or 1-butanol in the presence of triethylamine was used as the polymerization solvent. The resulting cis polymer was composed of a pseudohexagonal structure called columnar as π-conjugated self-assembly or π-conjugated self-organization in the solid state. The columnar polymer underwent isomerization from the predominant cis to trans form when compressed at 100 kg/cm^2 at room temperature. The pristine polymer and the compressed polymer were characterized in detail using ^{1}H NMR, wide-angle X-ray diffraction, laser Raman, electron spin resonance, and diffuse reflective UV−vis methods. Consequently, the data showed that the absorption maximum of the π-conjugated columnar polymer appears in an extremely longer wavelength region, i.e., at 490 nm, despite the cis form compared with 450 nm of the amorphous cis form. In the solid state, a large blue shift of the absorption maximum was found to be induced when the columnar structure was destroyed by compression to produce a trans−transoid form which has planar zigzag π-conjugation sequences. The pristine columnar polymer showed the $\lambda_{\max}$ as an entire absorption at notably longer wavelength so that the chromophore of the π-conjugated columnar polymer is not to be simply attributed to the primary structure, e.g., a repeated double−single bond structure, but rather should be ascribed to that of aggregated molecules called the π-conjugated columnar as self-assembly or self-organization. This explanation is a new concept with respect to the color of π-conjugated columnar polymers and is very important for the molecular design of electroluminescense (EL) and nonlinear optical (NLO) materials which are used at present in the solid state.

Introduction

In our previous reports[1−6] we have shown that cis-to-trans isomerization of poly((alkoxyphenyl)acetylene) bearing *o*- and *p*-alkoxy and *p*-nitro groups as the side chain in the phenyl ring, can be induced by compression at ca. 100 kg/cm^2 under vacuum even at room temperature, when these polymers are stereoregularly prepared using [Rh(NBD)Cl]$_2$ (NBD = norbornadiene) catalyst in the presence of triethylamine (TEA) or alcohol (ROH) as the polymerization solvent. We also reported that color of poly(phenylacetylene) (PPA)[7] and poly(p-methylphenyl)acetylene (PpMPA)[8] prepared using the Rh complex catalyst depends on the polymerization solvent used; e.g., alcohol or TEA solvent gives yellow polymer powders which are usually amorphous. On the other hand, orange or red polymer powders are obtained when the yellow polymers were immersed in toluene where a pseudohexagonal structure called columnar are formed as molecular assembly which has a fairly lower solubility in ordinary organic solvents. In this report we describe that poly(p-3-methylbutoxy)phenylacetylene (Pp3MBPA) stereospecifically prepared using the [Rh(NBD)Cl]$_2$ catalyst in the presence of the TEA solvent produces a pseudohexagonal structure called columnar polymer involving a cis−transoid structure in a relatively high yield, and compression of the columnar polymer resulted in not only decrease of the columnar content but also a large blue shift of the absorption maximum of the pristine polymer (see Scheme 1). Detailed characterization of the pristine and compressed Pp3MBPA polymers using ^{1}H NMR, wide-angle X-ray diffraction (XRD), electron spin resonance (ESR), diffuse reflective UV−vis (DRUV−vis), and laser Raman methods was performed before and after compression in order to correlate the polymer color with the columnar content. Conjugated polymers such as aromatic polyacetylenes,[6−9] e.g., the Pp3MBPA polymer, are potentially important materials not only from a scientific point of view but also for possible industrial applications, e.g., excellent photoconductive polymers,[10] model compounds of ferromagnetic polymers,[11,12] oxygen permeability,[9,13] humidity sensor,[14,15] nonlinear optical (NLO) polymers,[16,17] and promising electroluminescence (EL) polymers,[18] because the compression of the cis columnar polymer generates planar trans conjugated sequences.[1−6] It is also quite important to precisely control the properties of a solid polymer because the physicochemical properties of solid polymers are directly

Scheme 1

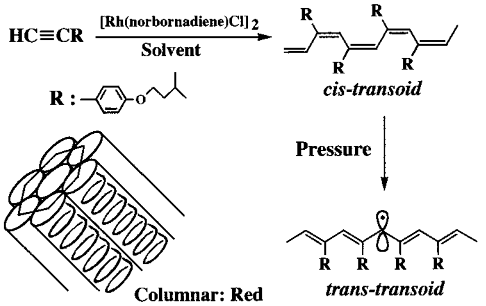

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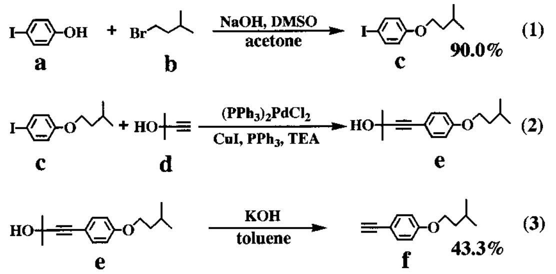
Table 1. Polymerization of (*p*-3-Methylbutoxy)phenylacetylene Using a Rh Complex Catalyst in the Presence of Various Solvents[a]

no.	[M]/[cat.]	solvent	time (h)	temp (°C)	yield (%)	M_n[b] × 10^4	M_w/M_n	color
1	150/1	EtOH[c]	2	20	96	9.9	2.66	yellow
2	150/1	water	2	20	70	23.1	2.23	orange
3	150/1	TEA	2	20	80	7.2	2.92	red
4	150/1	*n*-BuOH[c]	2	20	61	7.8	2.08	yellow
5	150/1	toluene[c]	2	20	21	2.5	2.04	yellow

[a] [M] = 0.20 mol/L. [b] Measured by GPC in chloroform using polystyrene as a standard. [c] TEA was used as the cocatalyst, [cocat.]/[cat.] = 100.

Scheme 2. Synthesis of *p*-(3-Methylbutoxy)phenylacetylene

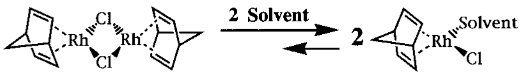


governed by the secondary structure, i.e., packing of the polymer chains. However, the control of the structure is not easy except for elongation of the solid polymer or formation of a superstructure such as columnar, found, for example, in poly(phenylacetylene),[7] poly(*p*-methylphenylacetylene),[8] and poly(alkylpropiolate).[14] The NLO properties, e.g., the third harmonic generation coefficient, $\chi^{(3)}$, are experimentally proven to be increased with increasing trans conjugation length.[19]

Experimental Section

Materials. All the solvents and products are reagent grade; the monomer, (*p*-3-methylbutoxy)phenylacetylene (p3MBPA), was prepared according to equations shown in Scheme 2. To a solution of 300 mL of acetone, 14.8 g (0.37 mol) of sodium hydroxide, 50 mL of dimethyl sulfoxide (DMSO), and 22.0 g (0.10 mol) of *p*-iodophenol (Aldrich) were added, and 25.0 g (0.17 mol) of *i*-amyl bromide (Tokyo Kasei) was added to the mixture and refluxed for 24 h. To the resulting solution 100 mL of ethyl ether was added to extract the product, and the product was washed with distillated water. The obtained organic layer was dried with anhydrous magnesium sulfate for 24 h, filtrated, and distillated (128 °C/0.6 mmHg); 26.1 g, yield 90.0%. The obtained *p*-isoamyloxyiodobenzene (26.1 g, 0.09 mol) was mixed with 300 mL of triethylamine, 0.111 g (1.5×10^{-4} mol) of dichlorobis(triphenylphosphine)palladium(II), 0.105 g (4.0×10^{-4} mol) of triphenylphosphine, and 0.099 g (5.2×10^{-4} mol) of copper(I) iodide and refluxed for 1 h under nitrogen. 13.0 g (0.15 mol) of 2-methyl-3-butyn-2-ol was added to the solution and refluxed for 3 h. After removal of the solvent using a rotary evaporator, ethyl ether was added to the product to extract the product. The obtained organic layer was washed with 300 mL of distillated water three times. The organic layer was dried with anhydrous magnesium sulfate for 24 h and filtrated, and the solvent was evaporated from the solution. The obtained product was used without further purification in the next step. The crude 4-*p*-(isoamyloxy)-phenyl-2-methyl-3-butyn-2-ol was refluxed in the presence of 50 mL of toluene and 1.70 g (0.03 mol) of potassium hydroxide for 4 h. After evaporation of the solvent from the resulting solution, 100 mL of ethyl ether was added to the solution to extract the product which was washed with 300 mL of distilled water. The obtained ether solution was dried with anhydrous magnesium sulfate for 24 h. After evaporation of the ethyl ether from the solution was distillated at 89 °C/0.2 mmHg to give the product, (*p*-3-methylbutoxy)phenylacetylene (7.4 g, 0.039 mol); yield 43.3%. The catalyst $[Rh(NBD)Cl]_2$ (NBD = norbornadiene) (Aldrich) was a commercial product and was used without any further purification.

Scheme 3



Polymerization. Poly(*p*-3-methylbutoxy)phenylacetylene (Pp3MBPA) was obtained by treatment of p3MBPA with the catalyst using different solvents and the same reaction conditions. In a typical procedure, 0.40 g (2.1×10^{-3} mol) of the monomer and the calculated amount of catalyst were dissolved in the solvent (TEA was dried according to conventional methods before use) in a U-shaped flask.[20] The reaction mixture was stirred according to time and temperature reported in Table 1. The reaction was stopped using an excess amount of methanol, and the polymer obtained was filtered off, washed with methanol, and dried under dynamic vacuum for 24 h. Yields are reported in Table 1. Elemental analysis of no. 1 in Table 1 as a typical polymer: Calcd (%) for $C_{13}H_{16}O_1$ (MW = 188.27): C, 82.94; H, 8.57. Found: C, 82.12; H, 8.63.

Analyses. Polymers were compressed at 100 or 200 kg/cm^2 for 10 min under dynamic vacuum at 10^{-2} mmHg at room temperature, using an oil press for manufacturing KBr disk after mixing with 200 mg of KBr and 2 mg of solid polymer. ESR spectra were recorded on a JEOL FE1XG with 100 kHz field modulation using a temperature control unit. Diffuse reflective UV−vis spectra of the polymer before and after compression were recorded on a JASCO V550 equipped with ISV-469. Laser Raman spectra were recorded on a JASCO TRS-401 using Ar^+ laser light at 514.5 nm. Gel permeation chromatography (GPC) of the polymer was determined with an JASCO GPC 900-1 instrument with a UV−vis detector using Shodex K-803L and K-806L columns, chloroform as eluent, and polystyrene as a standard. X-ray diffraction patterns were recorded on a JEOL JDX-3500 with a bent optical crystal monochromator.

Results and Discussion

Polymerization. *p*-3-Methylbutoxyphenylacetylene (p3MBPA) was polymerized using the Rh complex, $[Rh(NBD)Cl]_2$, as a catalyst in order to determine the best polymerization conditions. The polymerization results are shown in Table 1. It is clear that a good yield is obtained within 2 h even at 20 °C when ethanol or *n*-BuOH was used as the polymerization solvent in the presence of TEA. The obtained polymers were soluble in chloroform and tetrahydrofuran (THF) and insoluble in methanol and water. This suggests that alcohol, e.g., EtOH and *n*-BuOH, as the cosolvent in the presence of TEA can promote dissociation of the dimeric catalyst in order to generate a monomeric species as shown in Scheme 3.[21−23] The molecular weight of the polymer prepared using water as the polymerization solvent was the highest, $M_n = 23.1 \times 10^4$, among other polymers (see Table 1, no. 2), although TEA was not used in this case. This molecular weight is fairly large compared with that, i.e., M_n = 17 200, of poly(phenylacetylene) prepared using the same Rh complex catalyst in the

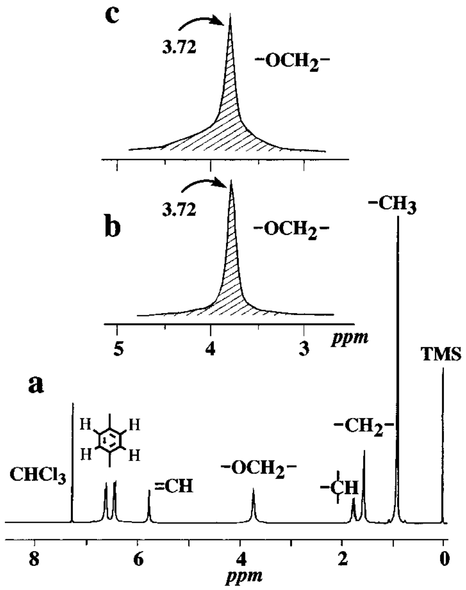


Figure 1. ^{1}H NMR spectra of Pp3MBPA polymers (Table 1, no. 3) prepared with [Rh(norbornadiene)Cl]$_2$ in the presence of triethylamine: (a) full scale spectrum of Pp3MBPA, (b) expanded peak of ∼OCH$_2$ proton before compression, and (c) expanded peak of ∼OCH$_2$ proton after compression at 100 kg/cm^2 under vacuum at room temperature.

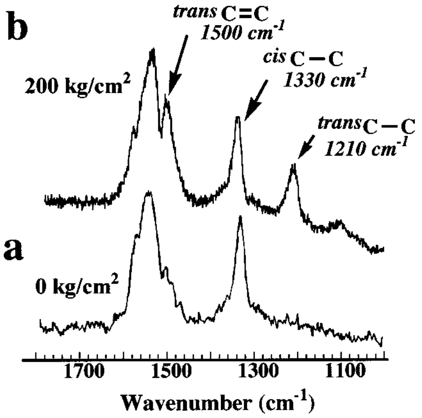


Figure 2. Laser Raman spectra of Pp3MBPA polymer (no. 3 in Table 1) observed at room temperature: (a) before and (b) after compression at 200 kg/cm^2 under vacuum at room temperature.

presence of water as the solvent.[24] This suggests that water also generate the monomeric species from the dimeric catalyst as shown in Scheme 3.[21−23] On the other hand, it seems that, in the case of the toluene solvent, the dissociation rate of the Rh catalyst is not high compared to those active solvents due to the low yield despite of presence of TEA.

^{1}H NMR. Figure 1a shows the ^{1}H NMR spectrum of poly(*p*-3-methylbutoxy)phenylacetylene (Pp3MBPA) with red color (Table 1, no. 3) observed in CDCl$_3$ solvent at 30 °C. The single peaks observed at 0.9 (6H), 1.7 (2H), 3.7 (2H), and 5.8 ppm (1H) were assigned to those of protons due to CH$_3$, CH$_2$, OCH$_2$, and =C−H groups, and a multiplet at 1.9 ppm (1H) was ascribed to that of the CH proton in the alkoxy group, and two doublets at 6.4 and 6.6 ppm can be assigned to those of the phenyl ring protons.[22] From Figure 1a it is clear that the cis isomer ratio can be estimated as almost 100% because the integral intensity ratio between the main chain =C−H proton and the −CH− or CH$_3$ proton in the alkoxy group is rigorously estimated as 1/1 or 1/3, respectively. This indicates that stereoregular polymerization of the corresponding polymer, i.e., no irregular sequences such as head-to-head and/or tail-to-tail structure, or a cyclohexadienyl moiety[25] as a result of intramolecular cyclization is induced to give such extremely sharp line width spectra despite cis π-conjugated sequences bearing molecular weight, e.g., $M_n = 7.2 \times 10^4$ as reported by us[23,26] and other group.[27] In the case of the yellow polymer (Table 1, no. 1), the ^{1}H NMR spectrum observed in the CDCl$_3$ solution was almost the same as that in Figure 1a, indicating that the difference of the color between them is not ascribed to that of the geometrical structure such as cis or trans form.

Compression. Polymer having a red color (see Table 1, no. 3) was compressed under vacuum at room temperature to determine whether cis-to-trans isomerization takes place. Figure 1b,c shows the expanded ^{1}H NMR spectra in the chemical shifts region due to ∼OCH$_2$∼ protons observed in CDCl$_3$ solvent before and after compression of the red polymer, respectively, although the whole spectrum having broader line widths observed after compression is not shown in those spectra. It should be noted, however, that each line width is increased to some extent compared with that of the original spectrum in the red polymer as shown in Figure 1a. This suggests that compression of the red polymer underwent the cis-to-trans isomerization to produce planar π-conjugated trans sequences which can stabilize unpaired electrons as mobile electrons called solitons as mentioned below. The compression can break the cis C=C double bonds rotationally in order to create two unpaired electrons as biradicals which can be spread as the π-radicals called solitons along the resulting trans planar sequences.[2,3] The ratio of trans sequences generated by compression could be estimated from the full scale spectrum of Figure 1b as ca. 11.3% comparing the areas of the CH_3 proton peak with that of the =C−H proton peak observed before and after compression. Therefore, the observed increase in each line width may be explained by not only the so-called magnetic dipole−dipole (DD) interaction between the polymer protons and the unpaired electrons but also the slower molecular motion of the resulting trans structure having planar π-conjugated sequences,[23,26] though the contribution ratio is difficult to quantitatively estimate. The ^{1}H NMR spectra shown in Figure 1b,c indicate that the resulting trans polymer is not reisomerized to the original cis isomer even when the obtained trans polymer was dissolved in the CDCl$_3$ solution at room temperature. Thus, on the basis of these data, it is concluded that the isomerization is an irreversible phenomenon, although the cis ratio which immediately reisomerized from the resulting trans isomer to the original cis isomer when the pressure was released cannot be estimated if such a reversible phenomenon quickly occurred in the case of our experiment. This isomerization phenomenon will be also proven by the ESR parameters observed after compression as mentioned below.

Laser Raman Spectra: Compression. Figure 2 shows laser Raman spectra of the pristine red polymer and compressed polymer observed using Ar$^+$ laser light at 514.5 nm. It is clear that, after compression, new peaks at 1210 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 2. The two peaks at 1500 and at 1210 cm^{-1} are assigned

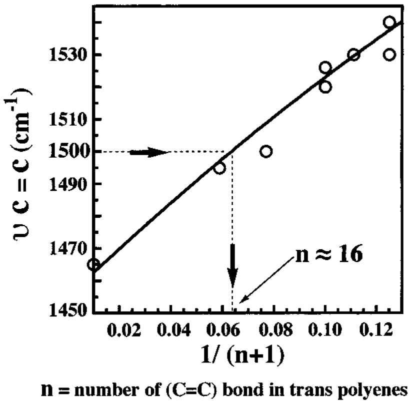


Figure 3. Dependence of the trans conjugation length, $(C{=}C)_n$, on the Raman peak of Pp3MBPA red polymer (Table 1, no. 3) prepared with $[Rh(norbornadiene)Cl]_2$ in the presence of triethylamine.

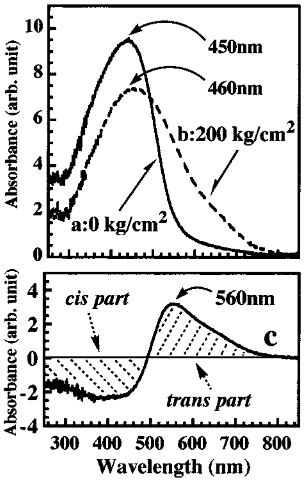


Figure 4. Diffuse reflective UV−vis spectra of Pp3MBPA yellow polymer (Table 1, no. 3) observed at room temperature: (a) before and (b) after compression at 200 kg/cm^2 under vacuum at room temperature; (c) the subtraction spectrum.

to those of the C═C bond and C−C bond vibrations in the resulting trans form, respectively.[1−6] The peak at 1330 cm^{-1} is assigned to that of 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.[26] The conjugation length was estimated to be $n \approx 16$ for 1500 cm^{-1}, assuming that the laser Raman peak of trans polyenes is correlated with the number, n, of the trans conjugation length, $(C{=}C)_n$,[28] as shown in Figure 3. Thus, it is suggested that compression of the resulting red polymer having cis−transoid form induced cis-to-trans isomerization even at room temperature in order to create such planar trans π-conjugated sequences.

We found that the pristine yellow Pp3MBPA polymer (Table 1, no.1) also showed almost the same Raman spectrum with that of the red polymer shown in Figure 2a. This strongly indicates that the yellow polymer even has also cis−transoid form.

Diffuse Reflective UV−vis: Compression. Figure 4 shows the DRUV−vis spectra observed before and after compression of the Pp3MBPA with yellow color (Table 1, no. 1) and the difference spectrum. The pristine yellow polymer showed an absorption maximum at 450 nm. The absorption maximum in the pristine yellow polymer was shifted to a higher wavelength side when compressed, i.e., from $\lambda_{max} = 450$ nm to $\lambda_{max} = 460$ nm, and the absorption intensity decreased. The difference spectrum obtained by subtraction of absorption spectra observed before and after compression at room temperature is shown in Figure 4c where a new absorption band is observed a higher wavelength. The band observed at 560 nm can be attributed to that of the trans conjugated sequences. The length of 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 Pp3MBPA yellow polymer[28] as shown in Figure 5. The trans conjugated lengths are estimated as ca. $n = 29$ as shown in Figure 5, and the data are shown in Table 2.

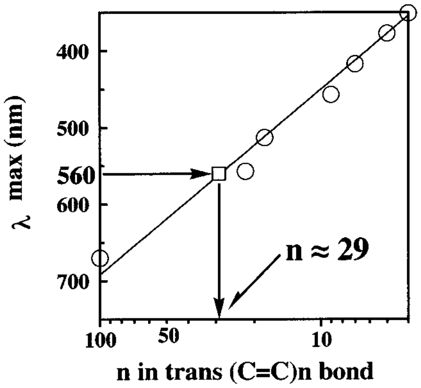


Figure 5. Dependence of the trans conjugation length, $(C{=}C)_n$, on the DRUV−vis peak of Pp3MBPA yellow polymer (Table 1, no. 1) observed after compression at room temperature.

Table 2. Absorption Maxima and π-Conjugation Lengths, $(C{=}C)_n$, Created by the Compression of Pp3MBPA Polymers at Room Temperature[a]

	abs max. (nm)				
no.	before		trans form	n in trans $(C{=}C)_n$	color
1	450	460	560	29	yellow[a]
3	490	450			red[a]

[a] Polymers (Table 1, nos. 1 and 3) were compressed under vacuum at ca. 10^{-2} Torr for 10 min.

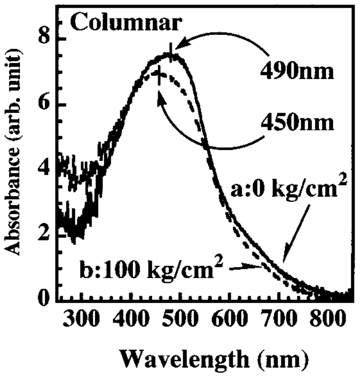


Figure 6. Diffuse reflective UV−vis spectra of Pp3MBPA red polymer (Table 1, no. 3) observed at room temperature: (a) before and (b) after compression at 100 kg/cm^2 under vacuum at room temperature.

Figure 6 shows DRUV−vis spectra observed before and after compression of Pp3MBPA polymer having red color under vacuum for 10 min at room temperature. It is clear that the red polymer gives a notably large absorption as an entire peak extending from ca. 300 nm to ca. 840 nm irrespective of the cis−transoid structure as mentioned above. It is noteworthy that such a long absorption tail was not observed in the poly(phenylacetylene)[7] and poly((methoxy and ethoxy phenyl)-acetylene)s[2,3] 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 regular structure as evidenced by the Raman spectral 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 (Table 1, nos. 1, 4, and 5) as shown below. A simple cis−transoid structure having sequences of one or two monomer units cannot allow us to explain why the λ_{max} must be observed at such a longer wavelength region, i.e., at 490 nm. Previously, we have shown that the amorphous yellow polymers, e.g., poly(*p*-methoxyphenylacetylene)[1,4] or poly(*p*-ethoxyphenylacetylene),[5] show the λ_{max} at ca. 440 nm, and the absorption maxima shifted to a longer wavelength, i.e., ca. 500−630 nm by compression to produce the planar π-conjugated sequences, associated with a small peak due to that of *p*-alkoxystyrene moieties.[4,5] On the other hand, in this experiment we also found that compression of the polymer bearing a red color resulted in a large blue shift of the absorption maximum from 490 to 450 nm, though a shoulder appears at a shorter wavelength region of less than 300 nm. Thus, compressions of the yellow and red polymer generate completely upside-down phenomena regarding the shift of the absorption maximum. However, 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 trans π-conjugated sequences. A small shoulder peak at less than 300 nm is also ascribed to that of the *p*-3-methoxybutylstyrene moiety[34] in the resulting trans form as reported as before.[1−6] Appearance of this small peak also suggests that the *p*-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.

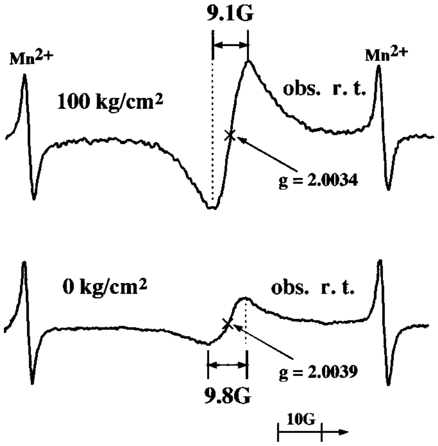


Figure 7. ESR spectra of Pp3MBPA polymer: (a) before and (b) after compression at 100 kg/cm^2 under vacuum at room temperature. Mn^{2+} shown in this figure is used as a standard signal of magnetic field.

Table 3. ESR Parameters Observed before and after Compression of Poly(3MBOPA) Polymerized in the Presence of TEA

press. (kg/cm^2)	*g* value	ΔH (G) room temp	ΔH (G) 77 K	spin (g) × 10^{16}
0	2.0039	9.8	10.4	1.1
100	2.0034	9.1	11.9	7.3

ESR Spectra. Previously, we have shown[1−6] that the *g* value of not only aromatic but also aliphatic polyacetylenes such as poly(alkylpropiolate)s called poly(acetylene ester)s can be used to deduce the exact geometrical conformations, i.e., cis form or trans form, when one heteroatom such an O, N, and halogen is substituted within the side chain of the polyacetylene molecules. Such a heteroatom has a relatively large spin−orbit coupling constant, δ,[29,30] compared with that of carbon, and the heteroatom 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 are nearly perpendicular where there is no strong magnetic interaction between the heteroatom 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 7). The observed parameters are shown in Table 3. It is clear that compression of the pristine red polymer decreases the *g* value from 2.0039 to 2.0034 and line width, ΔH_{msl}, from 9.8 to 9.1 G together with a large increase of the spin concentration from 1.1×10^{16} to 7.3×10^{16} spins/g, strongly supporting the compression-induced isomerization from cis form to trans form.[2−6] The compression of the polymer under vacuum can break the cis C═C double bonds to produce two radical spins as biradicals, and the resulting spins can stabilize in the resulting planar trans sequences as mobile unpaired electrons called solitons[32,33] 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., 9.1 G at room temperature and 11.9 G at 77 K just as shown in Table 3. 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.

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 the Pp3MBPA polymer is simply explained in terms of neither 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.[1−6] Therefore, it is concluded that a new chromophore as the entire peak bearing λ_{max} at 490 nm 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 similar to that of the so-called *J* aggregation of LB molecules.[35,36] This is a new and important concept because preparation of π-conjugated polymers having columnar structure is a new method to control

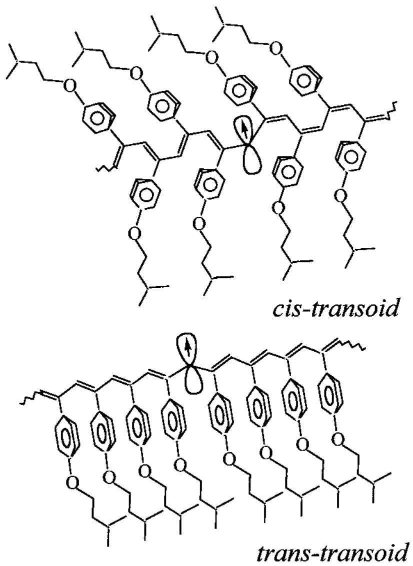


Figure 8. Perspective views of proposed *cis*−*transoid* and *trans*−*transoid* structures containing an unpaired electron.

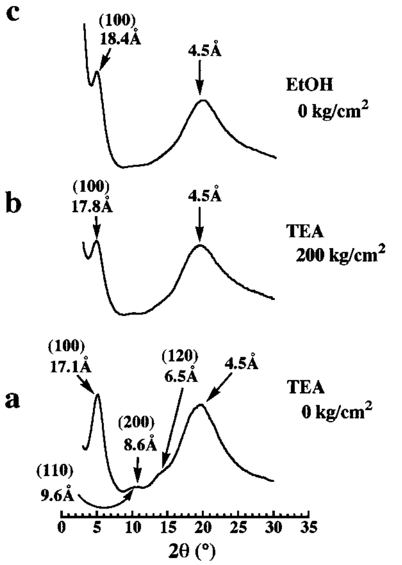


Figure 9. Wide-angle X-ray diffraction patterns observed at room temperature: (a) before and (b) after compression at 200 kg/cm^2 under vacuum at room temperature of Pp3MBPA polymer (Table 1, no. 3); (c) pristine yellow polymer (Table 1, no. 1).

the color of the conjugated polymer which can be used as new and promising advanced materials such as NLO or EL materials at the solid state.

X-ray Diffraction. We have shown that conjugated polyacetyelenes such as poly(phenylacetyelene),[7] poly(*p*-methylphenylacetylene),[8] and poly(alkylpropiolate)[9] called poly(acetylene ester)s, which were stereoregularly prepared with a [Rh(NBD)Cl]$_2$ catalyst, usually are constituted of a pseudohexagonal structure called columnar as π-conjugated self-assembly, and the columnar diameter depends on the side chain length of the polymer. We also examined the wide-angle X-ray diffraction pattern observed before and after compression of the red polymer which was prepared using TEA solvent (see Figure 9). The peaks observed at 17.1, ∼9.4, ∼8.6, 6.5, and 4.5 Å were analyzed, also assuming formation of a pseudohexagonal structure, i.e., columnar, though the (110) and (200) peaks are not clearly separated. Those peaks were attributed to the reflections of (100), (110), (200), (120), and amorphous halo, respectively. It is very clear that the compression of the red polymer decreased the intensity of the peak at (100) reflection to a great extent as shown in Figure 9a,b. 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. The content of the columnar of the yellow color polymer (Table 1, no. 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 polymer.

It is quite noteworthy, thus, that the columnar content of polyacetylenes prepared with the Rh complex catalyst is correlated with the color, i.e., λ_{max}. In other words, formation of such a columnar is a preferred method to shift the original absorption of the cis polymer to longer wavelength compared with that of the amorphous polymer without redesigning the polymer structure, although crystallinity of the columnar is related to the degree of aggregation states called π-conjugated self-assembly or self-organization as evidenced by data shown above.

As mentioned above, the PPA[7] and PpMPA[8] polymers, prepared with the Rh complex catalyst, were yellow and amorphous powders when a solvent, e.g., methanol, ethanol, 1-propanol, and TEA, was used in the polymerization. On the other hand, the orange or red polymers were obtained when cyclopentanol or cyclohexanol was used instead of those solvents, or the yellow polymers were immersed in toluene for 0.5 h at room temperature. Previously, we also proved that those orange or red polymers were composed of the columnar structure using the ESR and XRD methods.[7,8] It should be also noted, however, that color for poly(*n*-alkylpropiolate)s is correlated with those of the side chain length in the ester moieties where the columnar content is fairly high.[9,37] Thus, it is also concluded, therefore, that in these cases formation of the columnar is related to the color of the orange or red polymers and even in the cases of poly(*n*-alkylpropiolate)s. At present, the origin of the color of these aliphatic and aromatic polyacetylenes is examined more in detail together with the color of the cast film of the polymers, and the experiments regarding the pressure-induced cis-to-trans isomerization are in progress in our laboratory; the results will be published elsewhere soon.

Conclusion

Stereoregular polymerization of (*p*-3-methylbutoxy)phenylacetylene was successfully performed using the Rh complex, [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 or self-organization in high yields. The poly(*p*-3-methylbutoxy)phenylacetylene polymers obtained before and after compression 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 as the polymerization solvent manifested that the red color arises from that of the columnar as the π-conjugated self-assembly or self-organization 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 or self-organization of a conjugated polymer such as poly(*p*-3-methylbutoxy)phenylacetylene 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). 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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