Π-Conjugated Helical Nano-Columnar Polyacetylenes as Novel Color Controllable Materials

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Summary: A series of *p-n*-alkoxyphenylacetylenes (pROPA)s (R: C_nH_{2n+1}, n = 1, 2, 4, 6, 8, 10, 12, and 14) was polymerized with $[Rh(norbornadiene)Cl]_2$ catalyst in the presence of triethylamine to give stereoregular polyacetylenes, which colors of the resulting polymers were changed with increace of the carbon number of the alkyl side chains, i.e., yellow (n = 1∼6), orange (n = 8), red (n = 10), and dark red (n = 12, 14) along. Based on ^{1}H NMR and laser Raman spectra, it was found that the main chain of these polymers was cis-forms. Wide-angle X-ray diffraction (XRD) analysis indicated that yellow polymers were almost amorphous. In the case of the orange polymer, crystallinity, i.e., columnar content, was increased. Red and dark red polymers consisted largely of the columnar. It was concluded that colors of these polymers were strongly correlated with their columnar content. Therefore, the columnar of these stereoregular polyacetylenes can be considered as helical self-assembly π-conjugated , i.e., color controllable material.

Keywords: color; conjugated polymer; helix; polyacetylene; solid state structure

Introduction

Π-conjugated polymers have various colors which reflects its physical properties such as conductivities. It is very important to find control methods of their colors, i.e., absorption bands because these polymers can be applied in various fields of industry. Previously, we have shown that monosubstituted acetylenes such as phenylacetylene and its derivatives can be polymerized using a Rh complex catalyst, $[Rh(nbd)Cl]_2$, (nbd = norbornadiene) to selectively afford the corresponding polyacetylenes bearing a cis-transoid structure in high yields under quite mild conditions.[1–9] We also found that pseudohexagonal structure called a columnar as π-conjugate self-assembly is formed in the cases of poly(*n*-alkylpropiolate)s and poly(phenylacetylene) derivatives[7,8] prepared by the Rh complex catalyst in the presence of triethylamine or alcohol solvent as the cocatalyst. In this article, based on careful molecular design, we show color control method of stereoregular poly(*p*-alkoxyphenylacetylene)s through the side alkyl chain length together with detailed explanation on not only geometrical structure but also higher order structure in the solid state.

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Experimental Section

Materials

The *p*-substituted phenylacetylene monomers such as *p*-methoxy- (pMeOPA), *p*-ethoxy- (pEtOPA), *p-n*-butoxy- (pBuOPA), *p-n*-hexoxy- (pHexOPA), *p-n*-octoxy (pOctOPA), *p-n*-decanoxy (pC10OPA), *p-n*-dodecanoxy (pC12OPA), and *p-n*-tetradecanoxyphenylacetylene (pC14OPA) were prepared according to literature.[11] (Bicyclo [2.2.1]hepta-2,5-diene)chlororhodium(I) dimer ($[Rh(nbd)Cl]_2$) (Aldrich Co.) was

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used without further purification. Polymerization solvents were purified by conventional methods.

Polymerization Procedure

Polymerization was carried out using a U-type glass ampule equipped with two inlets capped with septum rubbers.[8] A typical polymerization procedure is as follows: 3 mmol of acetylene monomer (pROPA), which was prepared according to literature, and 0.02 mmol of $[Rh(nbd)Cl]_2$ together with 2 mmol of NEt_3 were dissolved in 7.5 mL of EtOH, respectively. After these solutions were placed in each side of the U-type ampule, the ampule was evacuated at 10^{-1} torr under dry ice temperature. After standing the solution for 10 min at the polymerization temperature, the monomer solution and the catalyst solution were mixed in order to start the polymerization reaction. After shaking for 2 h, the resulting polymer solution was poured into a large amount of methanol to precipitate a polymer powder (PpROPA), that was filtrated, and dried in vacuo at ca. 10^{-3} Torr for 24 h at room temperature.

Materials characterization

A number average molecular weight (Mn) and its molecular weight dispersity (Mw/Mn) of the resulting polymers were estimated by JASCO GPC 900-1 equipped with a refractive index detector using chloroform as an eluent at flow rate of 0.5 mL/min with a couple of Shodex K-806L column and calibrated with polystyrene standards at 40 °C. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-A 400II using chloroform-d as the solvent. Laser Raman spectra were recorded on JASCO TRS-401 using Ar^+ laser light at 514.5 nm. Diffuse reflective UV-vis spectra (DRUV-vis) were recorded on JASCO V-570 equipped using ISN-470. X-ray diffraction (XRD) patterns of powdered polymer were recorded on JEOL JDX-3500 with bent optical crystal monochrometor and using CuKα as a radiation source. All measurements were carried out at room temperature except for GPC measurement.

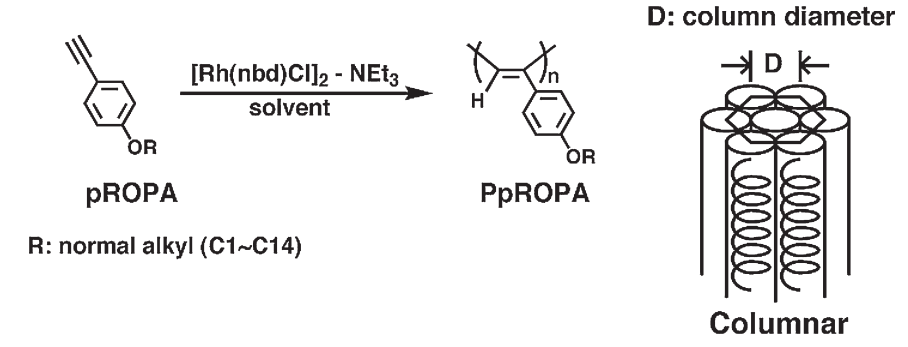
Results and Discussion

Rh Catalyzed Polymerization of Phenylacetylene Derivatives Having Various Alkoxy Chains

The pROPA monomers were polymerized by the Rh catalyst in EtOH as the polymerization solvent in the presence of NEt_3 as the cocatalyst (Scheme 1).[9] Yields and molecular weights were shown in Table 1. The obtained polymers showed variety of colors, i.e., yellow, orange, red, and dark red. The yellow polymers were soluble in $CHCl_3$ and THF, while polymers having other colors were partly soluble or insoluble in those solvents.

Diffuse Reflective UV-vis Spectra

In order to elucidate the difference of polymer color, i.e., absorption band, DRUV-vis spectra of these polymers were



Scheme 1.

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Table 1.
Polymerization of *p*-alkoxyphenylacetylenes by $[Rh(nbd)Cl]_2$.[a)]

No.	Monomer	[M] (mol/L)	Yield (%)	*Mn* (/10^4)	*Mw*/*Mn*	Color
1	pMeOPA	0.3	53	5.5	1.97	Yellow
2	pEtOPA	0.3	58	6.2	1.76	Yellow
3	pBuOPA	0.2	84	19.4	1.83	Yellow
4	pHexOPA	0.2	76	38.7	1.64	Yellow
5	pOctOPA	0.2	90	29.0[b)]	1.99[b)]	Orange
6	pC10OPA	0.2	88	-[c)]	-[c)]	Red
7	pC12OPA	0.2	84	-[c)]	-[c)]	Dark red
8	pC14OPA	0.2	78	-[c)]	-[c)]	Dark red

[a)] Polymerization conditions: 20 °C; 2 h; $[NEt_3]/[Rh\ cat.] = 100$.
[b)] Partly soluble in $CHCl_3$.
[c)] Insoluble in $CHCl_3$.

We have previously reported that pressure-induced and/or thearmal cis-to-trans isomerization of poly(phenylacetylene) derivatives are induced[4,11]. These phenomena can be correlated with conversion of main-chain from cis-transoid having shorter π-conjugation to trans-transoid having longer π-conjugation accompanied with red-shift of the absorption band. Additionally, it is very important to determine not only the geometrical structure of main-chain but also the higher-order structure, i.e., columnar content of these polymers. Because the crystallinity of the pristine PpROPA was also destroyed when the isomerizaiton took place.

measured (Figure 1). An absorption maximum: λmax of the yellow PpEtOPA was observed at 460 nm which was almost identical with those of other yellow polymers. In the case of the orange PpOctOPA, the λmax was red-shifted about 40 nm compared wiht the yellow PpEtOPA. On the other hand, the λmax of PpC12OPA was observed at very long wavelength region, 520 nm, whose large red-shift was never observed in other polymers. Thus, Table 1 shows that the absorption maximum, λmax of PpROPA is red shifted with increasing the carbon number in the alkoxy chain.

Geometrical Structures

It seems very important to decide the geometrical form of the relevant monosubstituted polyacetylenes with respect to possible four cis-transoid, cis-cisoid, trans-cisoid, and trans-transoid structures. Because the physicochemical properties of such π-conjugated polymers largely depend not only on main-chain structure but also higher-order structure which is composed of assembly of the polymer chain. In order to explain the difference of polymer color, the ^1H NMR and laser Raman spectra were adopted to determine the geometrical structures regarding the main-chain of the polymers.

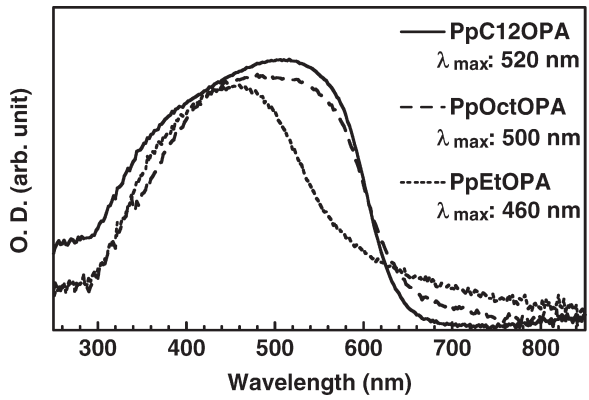

Figure 1.
Diffuse reflective UV-vis spectra of PpEtOPA, PpOctOPA, and PpC12OPA.

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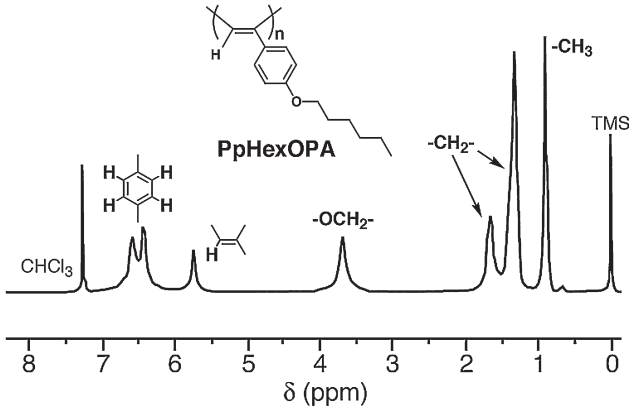

Figure 2.
^{1}H NMR spectrum of PpHexOPA observed at room temperature.

Figure 2 shows the ^{1}H NMR spectrum of poly(*p*-*n*-hexyloxyphenylacetylene), PpHexOPA observed in $CDCl_3$ solvent at room temperature as one of the typical spectrum of pROPAs. Seven proton signals were observed in the spectrum; a singlet peak at 0.8 ppm due to methyl group (3H), two singlet peaks at 1.4 and 1.7 ppm due to methylene group (8H), a singlet peak at 3.6 ppm due to methoxy group (2H), a singlet peak at 5.7 ppm due to vinyl protons (=C–H) in the cis-transoid sequence, and two singlet peaks at 6.4 and 6.6 ppm due to phenyl protons. It is noteworthy that ^{1}H NMR spectra of these polymers featured quite narrow and sharp line widths irrespective of fairly high molecular weight, e.g., $Mn =$ 387,000. This spectrum supports that these polymers have quite high stereoregular cis-transoid structure because the integrated peak intensity ratio of the vinyl proton, =C–H and the four phenyl protons was rigorously estimated as a quarter.[8,11,12]

Figure 3 shows the laser Raman spectra of the pristine PpMeOPA, PpHexOPA, and PpOctOPA. These spectral peaks were observed at the same positions responsible to the cis structure, irrespective of the carbon number in the side chain. This strongly suggests that the geometrical structure of these polymers were the same cis-transoid structure irrespective of different colors.[10] It may be, therefore, concluded that the difference of polymer color was responsible to the difference of higher-order structure in the solid state rather than geometrical structure.

Wide-angle X-ray diffraction (XRD)

We have shown that substituted polyacetylenes such as poly(alkylpropiolate), poly(*p*-methylphenylacetylene), and polyphenylacetylene which were stereoregularly prepared with a $[Rh(nbd)Cl]_2$ catalyst, usually can be composed of a pseudohexagonal structure called columnar as π-conjugated self-assembly at the solid state by using XRD, whose the columnar

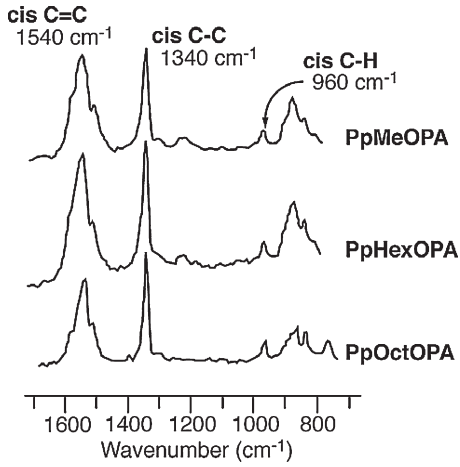

Figure 3.
Laser Raman spectra of PpMeOPA, PpHexOPA, and PpOctOPA.

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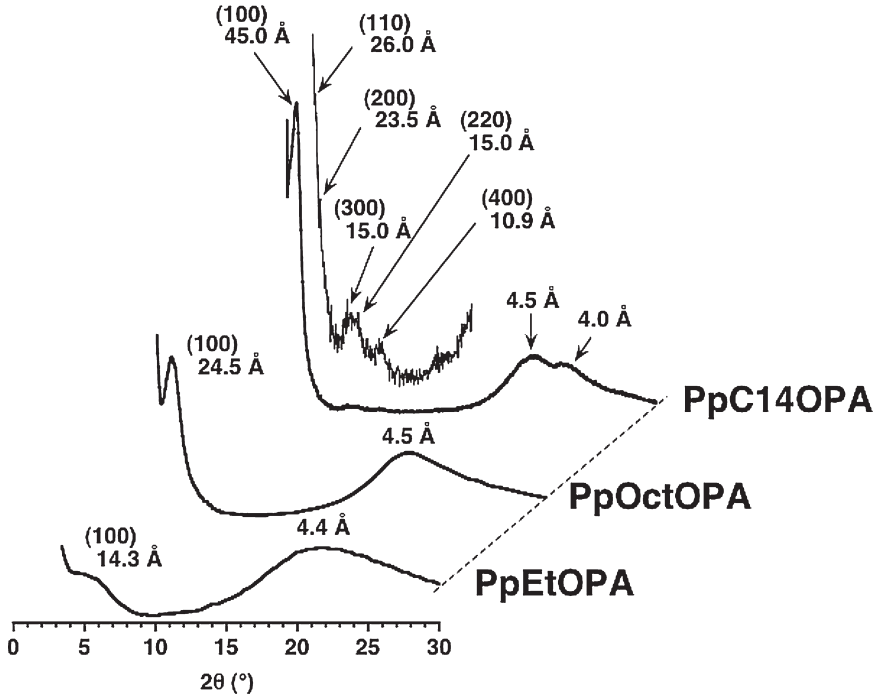

Figure 4.
XRD patterns of PpEtOPA, PpOctOPA, and PpC14OPA.

diameter depends on the side chain length of the polymer and their diameter is estimated as a nano size order: 1.3∼ 6.5 nm and the helical cis-transoid main-chain is packed in each column to stabilized the hexagonal column structure[7,8]. We also used the XRD method in order to determine relationship between polymer colors and higher-order structure, i.e., columnar. Figure 4 shows the XRD patterns of three polymers having different colors, such as yellow, orange, and dark red.

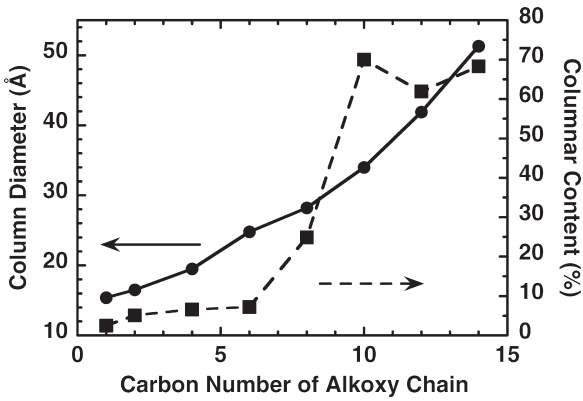

Figure 5.
Relationship with respect to column diameters, columnar contents, and carbon number of alkoxy chains on the phenyl rings of PpROPAs.

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The pattern of yellow PpEtOPA showed two broad peaks which can be assigned to (100) reflection of columnar and amorphous halo, respectively. A columnar content of the polymer, which was estimated in comparison with the area ratio of crystalline part and amorphous halo, was about 10%, suggesting that this polymer was almost amorphous. In the case of the orange PpOctOPA, a sharp (100) peak at 24.5 Å and amorphous halo were also observed. Since a sharp and strong (100) peak with several peaks was observed in the case of PpC14OPA, indicating clear formation of the columar and that its content was quite high content. The column diameters and the columnar contents of all the polymers estimated from their XRD patterns were summarized in Figure 5. The column diameter can be enlarged with increase of the carbon number of the side alkyl chain, the increasing rate of it over 8 of the carbon number was larger than that of below 6. The columnar contents increase slowly from the carbon number 1 to 6. However, the drastic increase of the contents start from the number 8 to 10, followed by the drop of the contents. The drop may mean intermolecular interaction i.e., formation of interdeditated structure between the alkyl chains. Furthermore, columnar contents may be correlated with their polymer colors because the λmax was red-shifted together with increase of the columnar contents[11,12]. It is, therefore, concluded that the columnar of stereoregular polyacetylene, i.e., helical π-conjugated self-assembly considerd as color controllable materials.

Conclusion

We have revealed that the stereospecific poly(*p*-*n*-alkoxyphenylacetylene)s prepared with a $[Rh(norbornadiene)Cl]_2$ catalyst in the presence of NEt_3 as the cocatalyst have cis form, regardless of the carbon number in the side alkyl chain. Colors of the resulting polymers were changed depending on the length of the side alkyl chain, accompanied by red-shift of the λmax when the polymer has longer alkyl chain, i.e., more than 8 as of the carbon number. Columnar contents were strongly correlated with their polymer colors because the λmax was red-shifted with increase of the columnar contents. It is, therefore, concluded that the columnar of stereoregular polyacetylene, i.e., helical π-conjugated self-assembly works as novel color controllable materials.

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