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Pressure-Induced Cis to Trans Isomerization of Poly((*p*-nitrophenyl)acetylene) Prepared Using Rh Complex Catalysts. Extension of π Conjugation Length

Rosaria D'Amato,[†] Takeyuki Sone,[‡] Masayoshi Tabata,*,[‡] Yoshikazu Sadahiro,[‡] Maria Vittoria Russo,[†] and Anita Furlani[†]

Department of Chemistry, University of Rome "La Sapienza", p.le Aldo Moro 5 00185 Rome, Italy, and Department of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628 Japan

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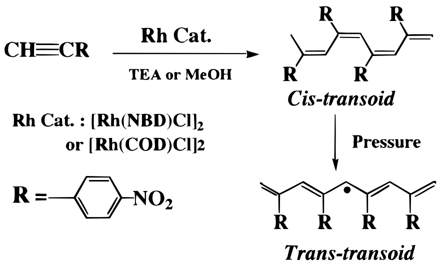
ABSTRACT: Stereoregular polymerization of (*p*-nitrophenyl)acetylene (pNPA) was performed using [Rh(norbornadiene)Cl]$_2$ and [Rh(cyclooctadiene)Cl]$_2$ catalysts to give poly((*p*-nitrophenyl)acetylene) (PpNPA), with a cis−transoid form under mild conditions. The polymer underwent isomerization from the predominant cis to trans form when compressed at 200 kg/cm^2 at room temperature. The polymers, obtained before and after compression, were characterized using IR, CP MAS ^{13}C NMR, ESR, and diffuse reflective UV methods. The data suggest that the isomerization of the resulting polymer from cis−transoid to trans−transoid form gives a conjugated trans planar zigzag structure. The trans conjugation lengths, n, in the polymer chain $(C{=}C)_n$ after the compression were estimated as ca. 29 or 50, when polymers obtained with methanol or triethylamine as the polymerization solvents were used. The trans sequence length obtained by thermal treatment of the cis−transoid polymer was also found to have less conjugated sequences than that of the compressed polymer. It is concluded, therefore, that the compression of the predominant cis−transoid PpNPA form gives longer conjugated trans sequences compared with that of the thermal isomerization of the pristine polymer.

Introduction

In our previous reports[1−6] we have shown that by compression at ca. 200 kg/cm^2 under vacuum even at room temperature cis to trans isomerization of poly((alkoxyphenyl)acetylene) bearing *o*-methoxy, *o*-ethoxy, and *p*-methoxy moieties as the side chain in the phenyl group can be induced. These polymers exhibit stereoregular structures when prepared in the presence of [Rh(norbornadiene)Cl]$_2$, [Rh(NBD)Cl]$_2$ catalyst, and triethylamine (TEA) or alcohol (ROH) as the polymerization solvent. We have now extended our investigations to the polymerization of pNPA together with the cis to trans isomerization of the resulting poly(*p*-nitrophenylacetylene) (PpNPA) induced by compression (see Scheme 1). Detailed characterization of the pristine and compressed PpNPA polymers using IR, CP MAS ^{13}C NMR, ESR, and diffuse reflective UV methods has been performed. Conjugated polymers such as the PpNPA polymer are potentially important materials not only from a scientific point of view but also for possible industrial applications, e.g., model compounds of ferromagnetic polymers,[7] oxygen permeability,[8,9] humidity sensors,[10,11] and nonlinear optical (NLO) properties.[12] It is quite important to control the properties of a solid polymer because the physicochemical properties of the solid are directly governed by the secondary structure, i.e., packing of the polymer chains. The control of the structure is not easy except for elongation of the solid polymer, or formation of superstructures such as columnar, found for example in poly(phenylacetylene),[13] poly((*p*-methylphenyl)acetylene),[14] and poly(alkyl propiolate),[14,18] can occur. The NLO properties, e.g., the third harmonic generation coefficient, $\chi^{(3)}$, are experimentally proven to be increased with increasing trans conjugation length:[15] *trans*-polyacetylene with planar conjugation sequences is preferred for the NLO materials. In this paper we report that the compression of PpNPA induces cis to trans isomerization: the generated trans planar conjugated sequence can improve the NLO properties of these materials (see Scheme 1). Mono- or disubstituted polyacetylenes with trans conjugated chains have been reported, but they have never been analyzed using unequivocal characterization methods such as ESR and UV spectra. We have studied the influence of compression of the *cis*-poly(phenylacetylene)s having a *p*-nitro group. Consequently, easy preparation of the trans-conjugated polyacetylene even at room temperature without heat treatment of the cis polymer at higher temperature was observed.[16]

Scheme 1



Experimental Section

Materials. All the solvents and products are reagent grade; the monomer *p*-nitrophenylacetylene (pNPA) was prepared according to a literature method;[17] the catalysts [Rh(COD)Cl]$_2$ (COD = 1,5-cyclooctadiene) and [Rh(NBD)Cl]$_2$ (NBD = norbornadiene) (Aldrich) were commercial products and were used without any further purification.

Poly((*p*-nitrophenyl)acetylene) (PpNPA) was obtained by reaction of pNPA with the catalyst using different solvents

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[†] University of Rome "La Sapienza".

[‡] Hokkaido University.

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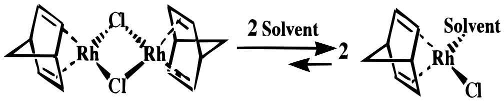
Table 1. Polymerization of (*p*-Nitrophenyl)acetylene Using Rh Complex Catalysts

no.	catalyst	[M]/[cat.]	solvent	time, h	temp, °C	yield, %	M_n[b]	M_w/M_n
1	$[Rh(NBD)Cl]_2$	50/1	MeOH	2	20	100	1300	1.60
2	$[Rh(NBD)Cl]_2$	10/1	MeOH	0.3	20	100	1200	1.08
3	$[Rh(COD)Cl]_2$	200/1	MeOH	24	50	70	2100	1.13
4	$[Rh(COD)Cl]_2$	200/1	MeOH[a]	24	50	80	2000	1.20
5	$[Rh(NBD)Cl]_2$	50/1	TEA	2	20	60	1500	1.45

[a] NaOH was added as the cocatalyst. The ratio of [NaOH]/[MeOH] was taken as 0.004. [b] Measured by GPC in tetrahydrofuran using polystyrene as a standard only for the tetrahydrofuran soluble part.

Scheme 2



and reaction conditions. In a typical procedure, 0.500 g (3.4 × 10^{-3} mol) of monomer and the calculated amount of catalyst were dissolved in the solvent (MeOH and Et_3N were dried according to conventional methods before use) in a U-shaped flask.[18] The reaction mixture was stirred according to time and temperature reported in Table 1. The reaction was stopped by adding 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 $C_8H_5NO_2$ (MW = 147.12): C, 65.31; H, 3.40; N, 9.52. Found: C, 63.22 H, 3.60 N, 8.97.

Polymers were compressed at 200 kg/cm^2 for 10 min under dynamic vacuum at 10^{-2} Torr at room temperature, using the manufacturing press for making a disk of solid polymer. ESR spectra were recorded on a JEOL FE1XG with 100 kHz field modulation using a temperature control unit. Diffuse reflective UV spectra of the polymer before and after compression were recorded on a JASCO V 550 equipped with ISV-469. CP MAS ^{13}C NMR spectra were recorded on a Brucker MSL 400. Gel permeation chromatography (GPC) of the soluble portion of the polymer was determined with an Eyela RI 10 instrument with an UV detector using Asahi columns, with tetrahydrofuran as an eluent and polystyrene as a standard.

Results and Discussion

p-Nitrophenylacetylene (pNPA) was polymerized using the Rh complexes $[Rh(NBD)Cl]_2$ and $[Rh(COD)Cl]_2$, which were found to be very active catalysts for similar monomers. The polymerization results are shown in Table 1. High yields are obtained even at 20 °C within 0.3 h when methanol was used as the polymerization solvent. The obtained polymers are slightly soluble in tetrahydrofuran and chloroform and insoluble in methanol and benzene. Very low molecular weight polymers could be obtained only on the soluble fractions (Table 1), but the insoluble fractions probably have higher molecular weights as reported before.[5] The insolubility may be ascribed to fairly strong aggregations between the inter- and/or intramolecular chains having highly stereoregular structures in the homopolymers. High polymerization yields were obtained, also decreasing the catalyst concentration to [M]/[catalyst] = 200/1 with $[Rh(COD)Cl]_2$ catalyst in the presence of NaOH as reported in our previous papers.[19-22] This suggests that methanol, reacting with NaOH, promotes dissociation of the dimeric catalyst and generates a monomeric species as shown in Scheme 2.

The IR spectra of the resulting polymers show no bands at 3252 cm^{-1} due to H−C≡ bond and at 2107 cm^{-1} of the C≡C bond characteristic of the monomer. The band at 1594 cm^{-1} can be attributed to the stretching vibrations of the C═C bonds in the main chain, indicating the formation of poly((*p*-nitrophenyl)acetylene) polymer by opening of the triple bonds. The stretching vibrations of the benzene rings fall at the same frequency as is observed in the IR spectra of the polyphenylacetylenes. In the CP MAS ^{13}C NMR spectrum of the resulting polymer the peak at ca. 147.4 ppm is assigned to a carbon carrying a NO_2 group, and multiplet peaks at 139.0 ppm are assigned to ═C− and ═CH carbons in the main chain and/or quaternary aromatic carbons connecting with the main chain. The peak at 127.8 ppm may be assigned to two ortho carbons carrying hydrogen. The peak at 122.8 ppm is also assigned to two meta carbons in the benzene ring, although the reliability of each peak intensity was lost because of TOSS pulse sequence,[23] and the solid NMR spectra of the insoluble parts in this polymer were the same as those of the soluble polymers.

ESR. *Pristine Polymer.* An ESR spectrum of homopolymer PpNPA was observed in order to determine the geometrical structure of the obtained polymers as the cases of poly((*p*- and *o*-methoxy)phenylacetylene)s,[1,3] poly((*o*-ethoxy)phenylacetylene),[2] and poly(alkyl propiolate)[24] polymers. The observed spectrum (polymer no. 3) is not symmetrical but extremely anisotropic as shown in Figure 1a. To the best of our knowledge, such unsymmetrical spectra have not been reported before for acetylene polymers. Therefore, the microwave power saturation effect[25] in the ESR spectrum of the PpNPA (Table 1, no. 3) was examined in order to determine whether this polymer is composed of an unsymmetrical component as an anisotropic spectrum or two components, e.g., cis and trans isomers. Figure 1 shows the microwave saturation effect of the PpNPA which was prepared using MeOH as the polymerization solvent. It is clear that the line shapes are changed with increasing microwave power. This suggests that the ESR spectrum observed in the pristine polymer is not composed of an anisotropic component, but at least two chemical species are present in this polymer sample, i.e., cis and trans geometrical isomers. Computer simulations[26] were performed, assuming that the triplet and singlet spectral components bearing different *g* values are each other superposed, and they are assigned to cis and trans conformers, respectively. The calculated spectra observed at 2 mW before compression are shown in Figure 1d, where a hyperfine coupling constant, a^{H_β} = 14 G, and $g = 2.0030$ are assumed for a triplet of the cis isomer, line width $\Delta H_{msl} = 12$ G and Gaussian line shape, and for a singlet of the trans isomer bearing $g = 2.0026$ and $\Delta H_{msl} = 6.0$ G. The singlet line, simulated with a Lorentzian line shape, suggests that the resulting trans isomer has planar trans zigzag conjugated sequences. This configuration stabilizes the π-radicals as mobile unpaired electrons called solitons as reported before.[1-3] The observed triplet cannot be ascribed to that configuration with a nitrogen radical in a nitro group but to a main chain carbon radical as in the case of poly((*p*- and *o*-methoxyphenyl)acetylene)s[3] and poly((*o*-

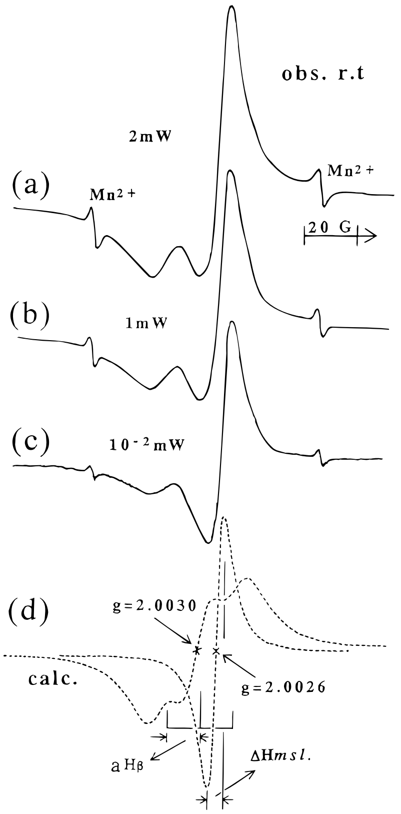


Figure 1. Microwave power saturation effect on the ESR spectra of PpNPA (polymer no. 3) observed at room temperature: 2 mW (a), 1 mW (b), 10^{-2} mW (c), and simulated spectrum (d). Mn^{2+} signals were used for internal standard of magnetic field.

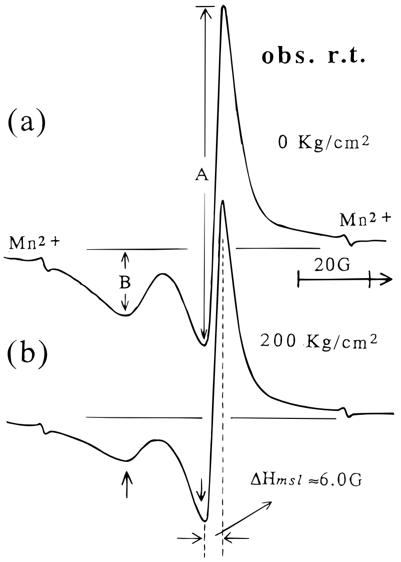
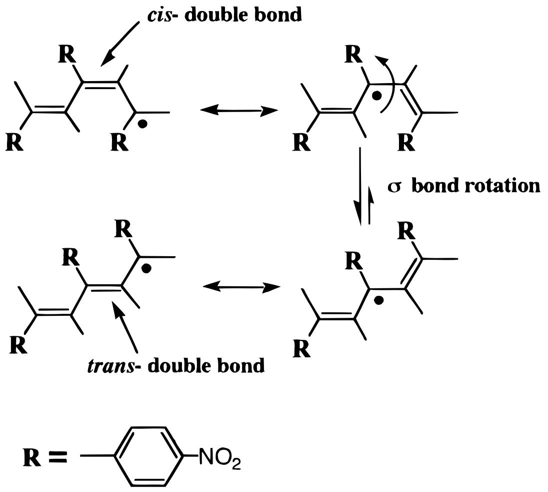


Figure 2. ESR spectra of PpNPA (polymer no. 3) observed before and after compression under vacuum at 10^{-2} Torr at room temperature: before compression (a) and after compression at 200 kg/cm^2 for 10 min (b).

ethoxyphenyl)acetylene)[2] as we will discuss later in this paper.

*Compression***.** Figure 2 shows ESR spectra observed before and after compression of PpNPA (Table 1, no. 3) under vacuum, ca. 10^{-2} Torr at room temperature; a different intensity ratio of lower field signal, *B*, and large central signal, *A*, is detected. The ratio *B*/*A* changed from 0.18 to 0.13 by compression in the spectrum recorded at 10^{-1} mW. This spectral change is ascribed to the pressure-induced cis to trans isomerization. This assignment is also supported by the fact that all the PpNPA polymers also have shown similar spectral changes. The large signal at higher magnetic field may be assigned to *trans*-polyacetylenes as in the cases of poly((alkoxyphenyl)acetylene)s as reported by us[1,2] and on the basis of the computer simulations mentioned above. The observed *g* value is estimated as ca. 2.0026, similar to that of hydrocarbon radicals of the unsubstituted polyacetylene,[27] suggesting that the *p*-nitrophenyl moiety in the trans polymer is perpendicular to the trans planar sequence whose conjugations is decoupled with the *p*-nitrophenyl moiety.[1,2] It was also found that the spectral intensity was increased by the compression, indicating increase of spin concentration from 1.05×10^{18} to 1.15×10^{18} spins/g as reported in the cases of poly((*o*- and *p*-methoxyphenyl)acetylene)s[1,3] and poly((*o*-ethoxyphenyl)acetylene).[2] Thus, the peak intensities of the large central signal and of the lower side signal, marked with arrows, partly reflect the content of cis–transoid and trans–transoid conformers, respectively.

Scheme 3



We also observed that the intensity of the triplet line increased by decreasing the polymerization temperature, indicating that the cis content of the polymer increases by decreasing the reaction temperature.

The pressure-induced cis to trans isomerization can be explained by radical mechanism because the radicals were detected before and after compression. It seems that the compression enhances the isomerization generating a smaller in volume trans conformer compared to the cis one, as shown in Schemes 1 and 3.

Polyacetylenes with higher content of cis conformer may give rise to the radical spins necessary to form an organo magnetic material because two radicals per one cis double bond may, in principle, be produced as a biradical when a π-bond in the cis C=C bond is broken as reported in our previous papers.[1,2]

Thermal Treatment. The influence of warming on the cis component of the polymer was invesigated. Figure 3 shows the temperature-dependent ESR spectra of PpNPA (Table 1, no. 1) subjected to heat treatment up to 175 °C under vacuum, using the temperature control unit. The ESR spectrum changed by the heat treatment from room temperature to 175 °C; in this temperature range, the polymer did not melt. The intensities of the lower field side peak and also of the middle field signal (marked with arrows in Figure 3a) decreased. The

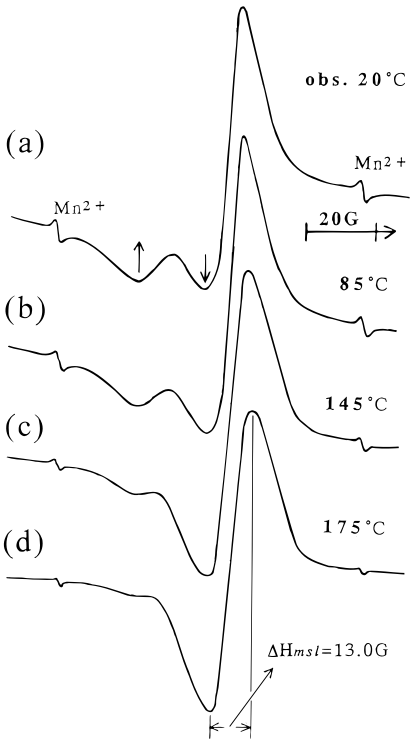


Figure 3. ESR spectra of PpNPA (polymer no. 1) observed at various temperatures: 20 (a), 85 (b), 145 (c), and 175 °C (d).

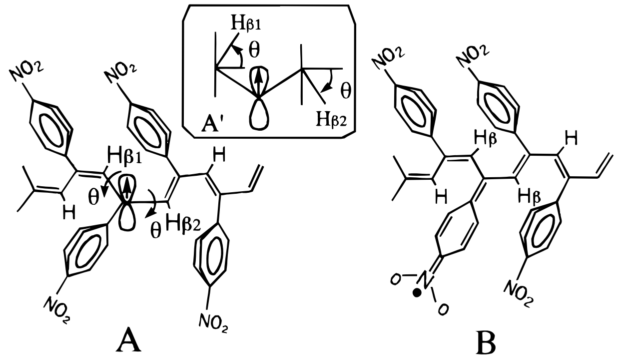


Figure 4. Proposed model compounds for vinyl carbon radical A and nitrogen radical B. The arrows show a twisted angle. The inserted illustration shows the dihedral angle θ between the unpaired electron and the H_β protons in the vinyl moieties.

triplet line disappeared by heating at 175 °C for a long time, indicating that the thermal cis–trans isomerization is induced. The heat treatment increased the line width, ΔH_{msl}, from 6 G after compression (see Figure 2) to 13 G, showing $g = 2.0027$. This suggests that in the resulting trans isomers the effective conjugation length was shorten by warming, although the thermal treatment does not induce cross-linking to destroy the cis sequence length. The formation of the short trans isomers called distorted or relaxed trans isomers is proven by the *g* value, 2.0027, observed after the thermal treatment as mentioned below.[2]

Conformational analysis using the so-called AM1 program[28] shows that the triplet line cannot be ascribed to the coupling with nitrogen (nuclear spin number $I = 1$) but to the coupling with the two nearest vinyl protons in the cis main chain: the possible conformer is proposed as A in Figure 4. A quinoid structure, whose unpaired electron is mainly localized in the nitro group, is also shown as B in Figure 4. The proposed A structure was energetically optimized using the program: the *p*-nitrophenyl ring is fairly perpendicular to the cis main chain, avoiding the delocalization of the unpaired electron, and the C–C bonds of the radical center are twisted as shown by arrows in Figure 4A. Therefore, the unpaired electrons may be delocalized with the two $H_{\beta 1}$ and $H_{\beta 2}$ protons to give the triplet line as observed in the Figures 1–3. The conformation A explains why the triplet line is not assigned to spin coupling with nitrogen but with the two vinyl protons of the cis form A. Using the AM1 calculation, the spin densities at the two protons, i.e., $H_{\beta 1}$ and $H_{\beta 2}$, were found to be not only equal but also the largest among the protons in the proposed model compound A, suggesting that the H_β protons give a fairly large hyperfine coupling constant as observed in our study. Further, the calculation indicated that a dihedral angle θ, between the orbital of the unpaired electron and those of the vinyl protons, is less than 90° as shown in Figure 4A. Thus, the AM1 calculation reasonably explains our experimental results.

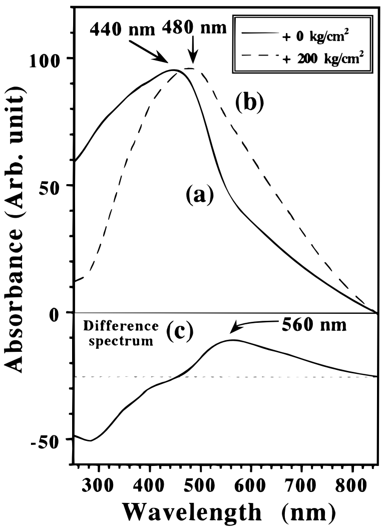


Figure 5. Diffuse reflective UV spectra of PpNPA (polymer no. 1) observed at room temperature: 0 kg/cm^2 (a), 200 kg/cm^2 (b), and (c) difference spectrum obtained by the subtraction of spectrum (b) from spectrum (a).

Diffuse Reflective UV. *Compression.* The diffuse reflective UV (DRUV) spectra of PpNPA before and after compression were examined in order to prove that the compression of the polymer induces the cis to trans isomerization shown by ESR measurements in analogy to the results reported by us in the case of poly((alkoxyphenyl)acetylene).[1–3] Figure 5 shows the DRUV spectra observed before and after compression of the PpNPA (Table 1, no.1) and the difference spectrum. The pristine polymer shows an absorption maximum at 440 nm with an absorption tail extending to more than 800 nm. It is noteworthy that such a long absorption tail was not observed in the poly(phenylacetylene) and poly((alkoxyphenyl) acetylene)s[2] which were prepared with the Rh complex catalyst, although it is observed in the PpNPA spectra. Absorptions at higher wavelengths (Figure 5a) are assigned to the trans conformer, suggesting that the trans sequences were already formed during polymerization even at low temperature, 20 °C. The absorption maximum in the pristine polymer is shifted to higher wavelengths by compression, i.e., from $\lambda_{\max} = 440$ nm to $\lambda_{\max} =$ ca. 480 nm. The difference spectrum obtained by subtraction of absorption spectra observed before and

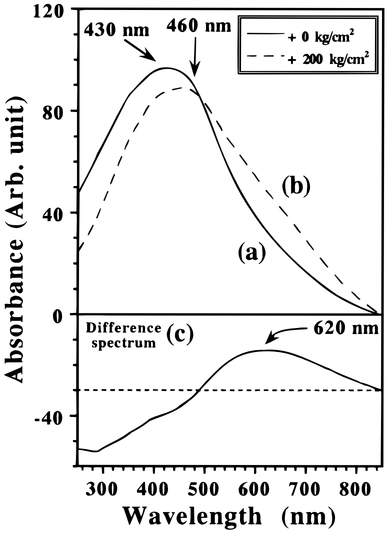


Figure 6. Diffuse reflective UV spectra of PpNPA (polymer no. 5) observed at room temperature. The compression at 0 kg/cm^2 (a), 200 kg/cm^2 (b), and (c) difference spectrum obtained by the subtraction of spectrum (b) from spectrum (a).

after compression at room temperature shows a new band at ca. 560 nm attributed to the trans conjugated sequences. We also found a larger shift of the absorption maximum by compression of the PpNPA (Table 1, no. 5) which was polymerized using triethylamine as the solvent. The spectra are shown in Figure 6 together with a difference spectrum. The $\lambda_{max} = 430$ nm of the pristine polymer was shifted to $\lambda_{max} =$ ca. 460 nm, indicating that λ_{max} of the difference spectrum is ca. 620 nm (Figure 6c). These absorption maxima observed after compression are at the highest wavelengths to our knowledge among the spectra of the monosubstituted aromatic polyacetylenes, e.g., poly[((*o*-trifluoromethyl)-phenyl)acetylene] (oTFMPA), 458 nm,[8] and poly[((*o*-trimethysilyl)phenyl)acetylene] (oTMSPA), 542 nm,[8,29] which were prepared with a Metathesis catalyst such as WCl_6. These absorption maxima suggest that the third harmonic generation coefficient, $\chi^{(3)}$, of the Rh polymer is larger than that of the polymer prepared with the metathesis catalyst,[12,15] as mentioned above. The length of conjugated trans sequences generated by the compression of PpNPA polymer was estimated using the so-called Shirakawa chart[30] where the relation between the sequence number of trans C=C bonds and UV absorption maxima in *trans*-polyenes is shown. The estimated trans conjugated lengths are shown in Figure 7, and the data are shown in Table 2.

*Thermal Treatment***.** We found that the thermal treatment of PpNPA (Table 1, no. 1) does not induce a red shift of the absorption maximum but a small shift to shorter wavelength from $\lambda_{max} = 440$ nm to $\lambda_{max} = 430$ nm as shown in Figure 8a,b. By the subtraction of the spectra observed before and after thermal treatment, as shown in Figure 8c, a new peak at ca. 400 nm appeared. This means that fairly short trans conjugated sequences are produced by the thermal treatment of the polymer, contrary to our expectation.[1−3] The trans sequence length is estimated as ca. $n = 6$ using the so-called Shirakawa chart.[30] However, the compression of the PpNPA after thermal treatment at 175 °C induced a shift of the λ_{max} from 430 to 460 nm, giving 570 nm as λ_{max} of the difference spectrum as shown in Figure 8c. The trans sequences produced by the heat treatment of the cis polymer are not planar forms but distorted or relaxed trans forms which have effective short conjugations as deduced by the ESR data above. It is noteworthy that the compression of the distorted trans polymer gave an absorption maximum at 570 nm. This is proven by the formation of ordered trans isomers resulting from the distorted trans isomers (Figures 8 and 9). It seems, however, that the thermal treatment of the cis polymer does not induce cross-linkings to disrupt the cis conjugation as precursors of the ordered or planar trans isomers. Thus, the DRUV data agreed with the ESR

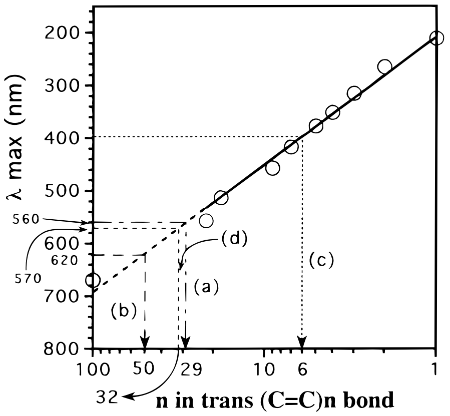


Figure 7. Relationship of the conjugation length, *n*, in trans double bond, $(C{=}C)_n$, and λ_{max} in the diffuse reflective UV spectra after compression of polymers no. 1 at 200 kg/cm^2 (a), after compression of polymer no. 5 at 200 kg/cm^2 (b), after heat treatment at 175 °C of polymer no. 1 (c), and after heat treatment at 175 °C after compression at 200 kg/cm^2 of polymer no. 1 (d).

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

no.	abs max. (nm) before	abs max. (nm) after	abs max. (nm) of trans form	*n* in trans $(C{=}C)_n$
1	440	480	560	29
4	430	460	620	50
1[a]	440	430	400	6
1[b]	430	460	570	32

[a] Polymer (Table 1, no. 1) was heat-treated at 175 °C under vacuum at ca. 10^{-2} Torr. [b] Polymer (Table 1, no. 1) was compressed after heat treatment at 175 °C under vacuum at ca. 10^{-2} Torr.

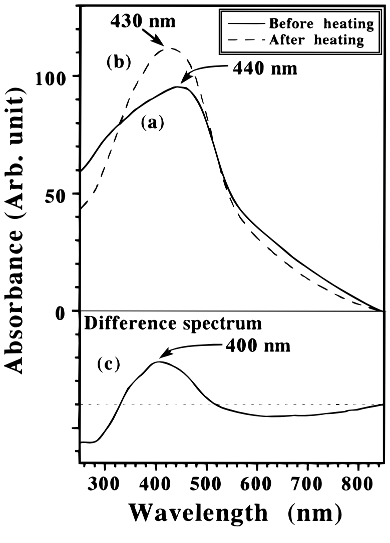


Figure 8. Diffuse reflective UV spectra observed before (a) and after (b) heating of PpNPA (polymer no. 1) under vacuum at 10^{-2} Torr. The difference spectrum is shown in (c).

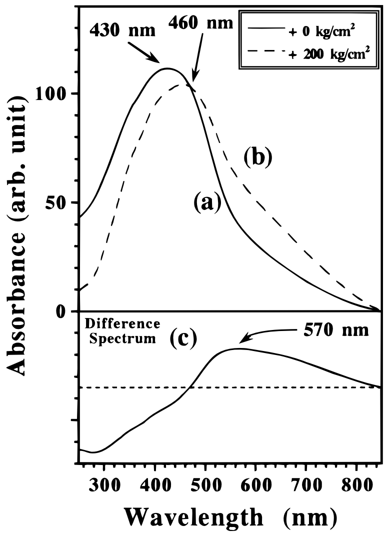


Figure 9. Diffuse reflective UV spectra observed before (a) and after (b) compression of the thermal treated PpNPA (polymer no. 1) at 175 °C and (c) difference spectrum obtained by the subtraction of spectrum (b) from spectrum (a).

spectral parameters, $\Delta H_{\mathrm{msl}} = 13$ G and $g = 2.0027$, observed after the thermal treatment at 175 °C as mentioned above.

The compression of PpNPA polymer, even at room temperature, is preferred in order to generate much longer trans conjugated sequences compared to that of the simple thermal treatment of the polymer. Thus, these data lead to conclude that the compression of the thermal treated polymer at ca. 175 °C produce ordered planar *trans* π conjugations to stabilize the mobile unpaired electrons.

Conclusion

The stereospecific polymerization of (*p*-nitrophenyl)-acetylene (pNPA) was successfully performed using [Rh-(NBD)Cl]$_2$ or [Rh(COD)Cl]$_2$ catalyst under various conditions to give rise to the cis−transoid isomer as the major component. The polymers obtained before and after compression were characterized in detail using IR, CP MAS ^{13}C NMR, ESR, and diffuse reflective UV. The compression of the cis polymer compared to the thermal treatment of the polymer is a suitable method to create long trans conjugated sequences through cis to trans isomerization.

We are currently studying the magnetic properties of the compressed polymers using a SQUID magnetometer. Trans aromatic polyacetylenes, other than PpNPA, also can be created by compression to generate potential useful planar trans conjugated sequences as promising NLO materials; investigations on this topics are in progress.

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