5200 *Macromolecules* **1997,** *30,* 5200−5204

Pressure-Induced Cis to Trans Isomerization of Aromatic Polyacetylenes. 2. Poly((*o*-ethoxyphenyl)acetylene) Stereoregularly Polymerized Using a Rh Complex Catalyst

Masayoshi Tabata,*,† Yoshiki Tanaka,† Yoshikazu Sadahiro,†
Takeyuki Sone,† Kazuaki Yokota,† and Ichiro Miura‡

Department of Molecular Chemistry, Graduate School of Engineering,
Hokkaido University, Sapporo 060 Japan, and Tokyo Instruments,
Edogawaku, Tokyo 134 Japan

Received May 28, 1996; Revised Manuscript Received June 19, 1997⊗

ABSTRACT: Stereoregular polymerization of (*o*-ethoxyphenyl)acetylenes (OEPA) was performed using a [Rh(norbornadiene)Cl]$_2$ catalyst in the presence of triethylamine to give poly((*o*-ethoxyphenyl)acetylene) (POEPA) bearing a cis-transoid form under mild conditions. The polymer underwent isomerization from the predominant cis form to the trans form when compressed at 200 kg/cm^2 at room temperature. The polymers, obtained before and after the compression, were characterized in detail using laser Raman, diffuse reflective UV, ESR, and X-ray diffraction. The data suggested that the isomerization of the resulting polymer from the cis-transoid to the trans-transoid form was induced to give rise to the conjugated trans-planar zigzag structures, where unpaired electrons are stabilized as mobile electrons called solitons. The formation of the soliton radicals was confirmed by the motional narrowing of the line width observed in the ESR spectra of the compressed polymer. The trans conjugation length, *n*, $(C{=}C)_n$ generated by the compression was estimated as n = *ca*. 22−45 using UV and laser Raman. The studies show that the compression of the cis-transoid POEPA form is the preferred method to isomerize it to the trans-transoid form. The compressed polymer contains a higher degree of conjugation compared with that of the thermal isomerization of the pristine polymer.

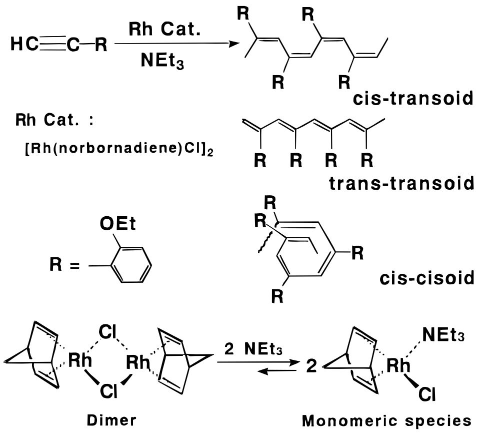
Introduction

We have reported the highly stereoregular polymerizations of (*m*-chlorophenyl)acetylene (mCPA),[1] its homologues,[2] and alkyl propiolates[3] catalyzed by a Rh complex, i.e., [Rh(norbornadiene)Cl]$_2$, [Rh(NBD)Cl]$_2$, in the presence of triethylamine (TEA) or alcohol as well as our studies on the mechanism of the polymerization.[4] The polymers, which have cis-transoid forms, were selectively formed in high yields under mild conditions. In further studies we revealed that the polymerization of pentynoate bearing a cholesteric mesogen,[5] synthesis of an ultra-high-molecular-weight poly(phenylacetylene) (UHMW PPA), M_w *ca*, 4. 30 × 10^6,[2] and copolymerization between monomers bearing electron donor and acceptor groups[6] are achieved by the Rh catalyst. We also reported the thermal-induced radical spin generation through the rotational scission of the cis C=C bond in the cis-transoid polymers[7,8] and aggregations of the radical spins as spin self-assemblies through the solvent induced columnar formations.[2,9a−c,]

We proposed that triethylamine or alcohol causes the dissociation of the binuclear complex, [Rh(NBD)Cl]$_2$ into the monomeric species which may, in turn, function as an important initiation species for this polymerization[1,2,4] as shown in Scheme 1.

There appear to be marked structural as well as physicochemical differences between polymers prepared with the Rh complex vs those prepared using metathesis catalysts, e.g., WCl$_6$, as evidenced by NMR,[5] ESR,[7,8] and laser Raman methods.[5] A unique feature of the polymer prepared using the Rh complex is formation of pseudo-hexagonal-packed structures, self-organizations which have long-range positional order along the molecular axis.[3,9]

Scheme 1



As a result of the above studies, we performed the polymerization of the (*o*-ethoxyphenyl)acetylene (OEPA) monomer, which contains a bulky *o*-ethoxy group, using the active and stereospecific Rh catalyst in the presence of a strong amine. In the course of measurement of the resonance Raman (RR) spectra of the POEPA we noted that the POEPA polymer, which initially was orange in color, changed to a dark-red color when it was compressed for preparation of a KBr disk. We concluded that this change corresponded to the isomerization of POEPA from cis-transoid form to trans-transoid form. In this paper, we wish to report further studies on the pressure-induced isomerization of the cis POEPA to the trans POEPA form, along with detailed characterization of the POEPA using diffuse reflection UV, laser Raman spectroscopy, ESR, and wide-angle X-ray diffraction.

To the best of our knowledge, no report on the polymerization of the OEPA monomer, including the pressure-induced cis−trans isomerization of the resulting poly((*o*-ethoxyphenyl)acetylene), has appeared, al-

---

† Hokkaido University.

‡ Tokyo Instruments.

⊗ Abstract published in *Advance ACS Abstracts,* August 15, 1997.

S0024-9297(96)00766-8 CCC: $14.00

Table 1. Polymerization Results of (*o*-Ethoxyphenyl)acetylene Polymerized with the Rh Complex, $[Rh(NBD)Cl]_2$ in the Presence of Various Solvents[a]

no.	catalyst	[M], mol/L	time, h	solvent	yield, %	M_n[b]	M_w/M_n
1	$[Rh(NBD)Cl]_2$	0.5	1.0	THF	90.6	2900	1.96
2	$[Rh(NBD)Cl]_2$	0.2	4.0	$CHCl_3$	58.8	3800	1.94
3	$[Rh(NBD)Cl]_2$	0.5	4.0	TEA	80.6	*d*	
4	$[Rh(NBD)Cl]_2$	0.5	24.0	TEA	91.6	*d*	
5	WCl_6·*n*-Bu_4Sn[c]	1.0	16.0	toluene	trace		

[a] Polymerized at 30 °C under N_2 atmosphere; [M]/[Cat] = 100; [Cocat]/[Cat] = 100. [b] Measured by GPC in chloroform using polystyrene as a standard only for the $CHCl_3$-soluble part. [c] Catalyst, WCl_6; cocatalyst, *n*-Bu_4Sn; [M]/[Cat] = 100; [Cocat]/[Cat] = 1. [d] Insoluble in chloroform.

though a preliminary communication on poly((*o*-methoxyphenyl)acetylene), POMPA, was reported by us.[10]

Conjugated polymers such as polyacetylenes are potentially important from the standpoint of not only basic chemistry but also industrial potential. Model compounds having an oxygen permeability,[11,12] ferromagnetic property,[13] and nonlinear optical properties[14] have been reported.

Experimental Section

Materials. (*o*-Ethoxyphenyl)acetylene was prepared from *o*-aminophenetidine, i.e., (*o*-ethoxyamino)benzene according to a method similar to that used for (*o*-methoxyphenyl)acetylene.[10]

The yield of the monomer, (*o*-ethoxyphenyl)acetylene (OEPA), was 44% (50 °C/5 mmHg). The detailed preparation method of the monomer will be published elsewhere.

Polymerization. After the treatment of 5.0×10^{-1} mol of OEPA with 5.0×10^{-3} mol of $[Rh(NBD)Cl]_2$ in 1 L of various solvents at 30 °C for 24 h, poly((*o*-ethoxyphenyl)acetylene), POEPA was obtained in relatively high yield as a fine orange powder although the polymer was partly soluble in chloroform and tetrahydrofuran and insoluble in methanol.

Anal. Calcd for $C_{10}H_{11}O_1$(147.19): C, 82.15; H, 6.89; Found: C, 81.89, H, 7.05.

Gel permeation chromatography of the soluble portion of the polymer was estimated using chloroform as eluent. Laser Raman spectra were run on a Renishow Ramascope 2000 using KBr pellets. Wide-angle X-ray diffraction (WAXD) were recorded by JEOL JDX 8020 at room temperature using Ni-filtered Cu Kα radiation. Electron spin resonance(ESR) spectra were recorded on a JEOL FE1XG with 100 kHz field modulation equipped with a temperature control unit from room temperature to 77 K.

Results and Discussion

Table 1 shows the results of polymerization of the OEPA monomer initiated by the Rh complex catalyst using various solvents. The highest yield was obtained when TEA was used as the polymerization solvent although these polymers were partly soluble in chloroform, tetrahydrofuran(THF), and insoluble in methanol.

Figure 1 shows the resonance Raman (RR) spectra observed before and after compression (100 kg/cm²) of the POEPA polymer (No. 4 in Table 1) using a $He-Ne^+$ laser of wavelength 632.8 nm. The peak at 1553 cm^{-1} observed before the compression is assigned to that of C=C bond stretching in the cis polyacetylene, although the peak is overlapped with that of the phenyl ring.[15-17] The sharp peak at 1338 cm^{-1} is assigned to the cis C−C bond coupled with the single bond connecting the main chain and phenyl ring.[15-17] It is seen that pressure induced to shift the peak at 1553 cm^{-1} to the lower wavelength side with decreasing intensity as shown in Figure 1b. This suggests that the ratio of the cis component is decreased by the pressure. Interestingly, compression increased the intensity of the peaks at 1487, 1475, and 1191 cm^{-1} and inversely decreased the intensity of the peaks at 1533 and 960 cm^{-1}, which are assigned to the cis C=C bond and C−H deformation of the cis form, respectively.

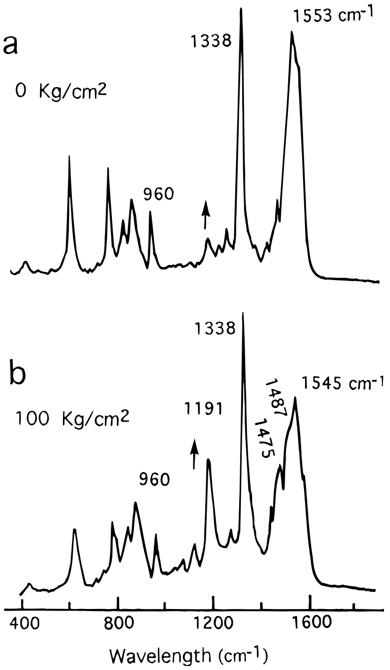


Figure 1. Resonance Raman spectra of POEPA polymers observed at room temperature: (a) before compression; (b) after compression at 100 kg/cm².

The peaks at 1487 and 1475 cm^{-1} generated by the compression are attributed to the trans C=C bond bearing a considerably long trans-conjugated length.[15-17] The peak at 1191 cm^{-1} is assigned to the vibrational band of the C−C bond in the trans chain, coupled with that of the C−H bond in the C=C−H group. This peak is observed in poly(phenylacetylene) (PPA) derivatives bearing a fairly long trans sequence which was obtained by γ-ray irradiation of the phenylacetylene derivative in the solid state.[8]

Thus, the peaks of the RR spectra observed after the compression are characteristic of the *trans*-polyacetylenes synthesized by Shirakawa et al.,[17] and consistent with the hypothesis that the compression of POEPA results in a conversion of the cis to the trans form which may be incorporated in the original cis sequence. It is noteworthy that the increase in the intensity of the peaks observed at 1487−1475 and 1191 cm^{-1} and the decrease in the intensity of the peak at 960 cm^{-1} stopped at pressures of about 200 kg/cm², although a much higher pressure, i.e., 500 kg/cm², was exerted on the sample. Further support for the assignments derives from the fact that the poly[((*o*-(trimethylsilyl)phenyl)-acetylene)], PTMSPA,[12,18] polymerized with WCl_6, which has a dark violet color and which is known to be an oxygen-permeable material, showed a RR spectrum quite similar to that of the POEPA compressed polymer (see Figure 1b) and the compression did not induce the RR spectral change appreciably even at 10 000 kg/cm². These facts suggest that the PTMSPA polymerized with the so-called metathesis catalysts, WCl_6 or $MoCl_5$,[12,18] is composed of a trans-conjugated sequence as the major component as is generally believed. This also indicates that the polymer with the trans sequence is not converted to the cis form on compression owing to thermodynamic preference as has been believed.

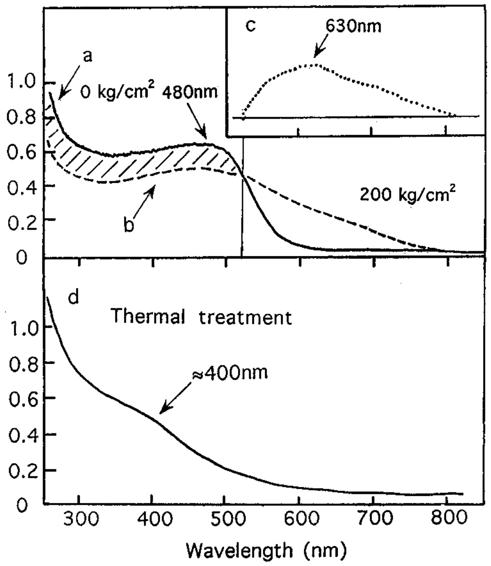


Figure 2. UV spectra of POEPA polymers observed at room temperature. The compression at (a) 0 kg/cm^2 and (b) 200 kg/cm^2, the (c) longer wave region spectrum obtained by the subtraction of part a from part b and (d) the UV spectrum observed after the heat treatment at 237 °C.

To the best of our knowledge, mono- or disubstituted polyacetylenes with complete trans-conjugated chains have not been reported, nor have they been analyzed using a unequivocal characterization method such as laser Raman spectra. Therefore, the compression of the *cis*-polyacetylenes with substituent groups is of potential importance since it enables easy preparation of the trans-conjugated polyacetylene at room temperature without heat treatment of the cis polymer at higher temperature.[7,19]

UV Spectra. UV spectra were observed in order to determine the conjugated sequences obtained before and after the compression using the diffusive reflection method. The sample was measured after mixing with 200 mg of γ-alumina, Al_2O_3, and 1 mg of the polymer. The spectra are shown in Figure 2a. The absorption maximum, λ_{max} of the pristine polymer before compression, appears at around 480 nm as a rather broad peak. The line shape of the absorption changed, i.e., the absorption has a very broad shoulder at higher wavelength region which extends up to *ca.* 800 nm when 200 kg/cm^2 pressure was exerted on the polymer under vacuum at *ca.* 10^{-2} Torr as shown in Figure 2b. It was also found, however, that the absorption maximum was further shifted to 500 nm when the pressure was increased from 200 to 500 kg/cm^2, but the spectral shape at the longer wavelength region remained unchanged. A spectral subtraction of Figure 2a from Figure 2b was carried out in order to obtain the longer wavelength band generated by the compression and the obtained spectrum is incorporated as Figure 2c in the same figure where the dotted line has a λ_{max} at *ca.* 630 nm. Thus, we were able to assign the new absorption peak at *ca.* λ_{max} = 630 nm to that of the trans-conjugated polymer. Further, the absorption region with slant lines as shown in Figure 2 may be approximately ascribed to that of the reduced cis form which should be transformed to that of the trans-conjugated sequences. This assignment may be supported by the facts that this λ_{max} is the largest absorption maximum among the monosubstituted aromatic polyacetylenes which have been prepared: e. g., poly[((*o*-(trifluoromethyl)phenyl)acetylene)] (OTFMPA),[12] 458 nm; poly[((*o*-trimethylsilyl)phenyl)-acetylene)] (OTMSPA),[12,18] 542 nm.

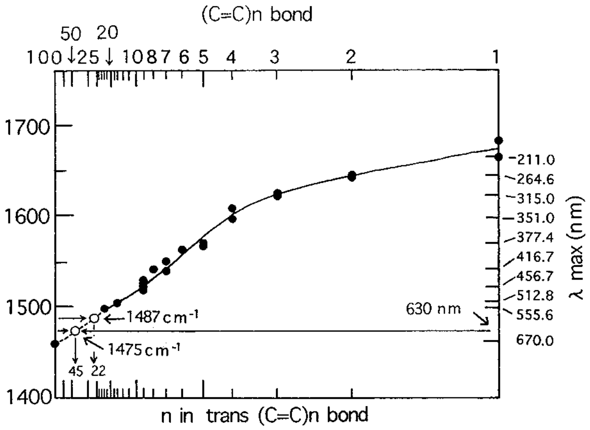


Figure 3. Shirakawa's relations with respect to the sequence length number of trans C=C bonds for UV absorption maximum in the trans polyene and resonance Raman spectral peaks.

Thermal Isomerization. Thermal isomerization of the POEPA polymer was also performed in order to compare the absorption spectrum with that of the compressed POEPA polymer using a shielded glass ampule at 237 °C under vacuum, 10^{-3} Torr. The spectrum observed in the thermally isomerized polymer is also shown in Figure 2d in which a bare shoulder appeared at *ca.* 400 nm. It is clear that the thermal isomerization does not induce a shift of the absorption maximum to a longer wavelength, but instead, it is inversely shifted to a shorter wavelength. This may show formation of a less conjugated trans sequence unlike the case of the compressed polymer. Thus, the compression of the ortho-substituted phenylacetylene appeared to be the preferred method to shift the absorption maximum to a longer wavelength where more conjugated trans sequences are formed. This indicates that planar trans conjugation lengths are preferentially produced if the *o*-ethoxybenzene moiety in the POEPA polymer is twisted out of the planar trans zigzag conjugation in order to give rise to the rather longer wave absorption maximum, *ca.* 630 nm. On the other hand, the conjugation form produced by the thermal isomerization does not contain such planar trans sequences but, instead, a fairly twisted polymer chain form whose structures do not absorb at longer wavelengths as deduced by the UV spectrum in the Figure 2d.

These results lead us to conclude that the side chain in the POEPA polymer obtained after the compression does not contribute to the shift to longer wavelength but functions as simple protons analogous to the nonsubstituted polyacetylene.[15,17] Therefore, the trans conjugation length, $(C{=}C)_n$, formed by the compression can be estimated to be n = *ca.* 45 because Shirakawa's chart[5,17] can be used to estimate the $(C{=}C)_n$ length as shown in Figure 3. Inspection of this chart also shows that the conjugation length can also be estimated as n = *ca.* 22−45 from the peak, *ca.* 1475−1487 cm^{-1}, observed in the Raman spectra. Therefore, the conjugation lengths estimated by the laser Raman method are in reasonably agreement with that of the conjugation length estimated using the UV method.

ESR Spectra. The ESR spectra of POEPA before and after the compression were observed in order to determine if the conformational change with increase of radical concentration is induced by pressure; the spectra at various pressures are shown in Figure 4, together with a computer-simulated spectrum. The ESR parameters, i.e., line width, $\Delta Hmsl$, and g value

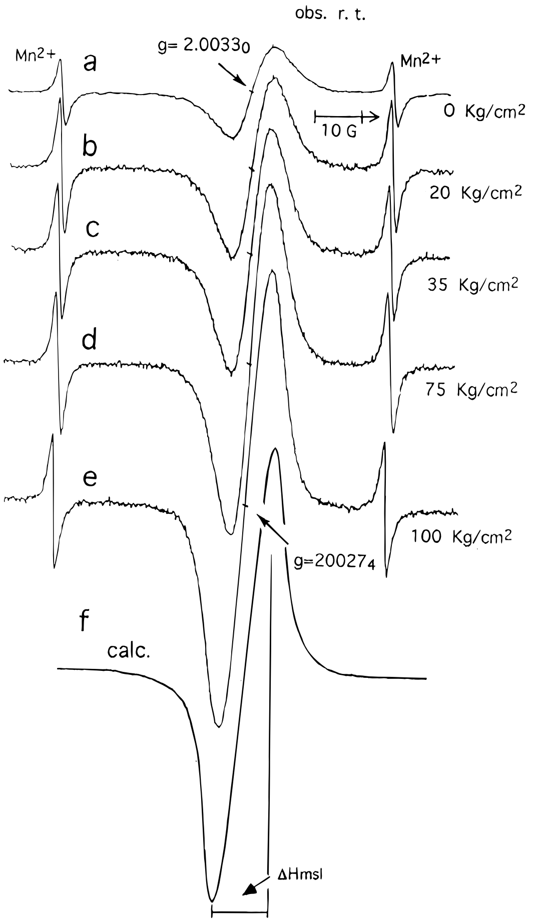


Figure 4. Pressure dependence of ESR spectra observed in the POEPA polymer at room temperature: (a) 0, (b) 20, (c) 35, (d) 75, and (e) 100 kg/cm^2 and (f) simulated spectrum.

Table 2. Pressure Dependences of ESR Parameters Observed in the POEPA Polymer at 300 and 77 K, Respectively[a]

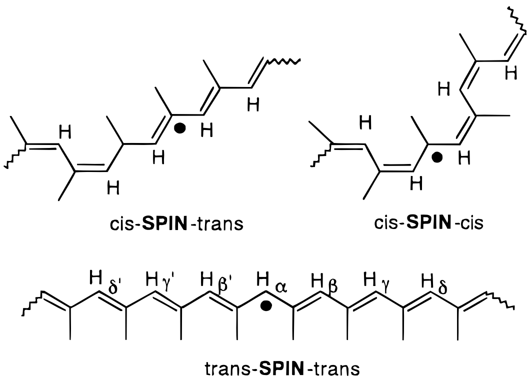
		300 K		77 K	
no.	pressure, kg/cm^2	g value	$\Delta Hmsl$, G	g value	$\Delta Hmsl$, G
0	0	2.0033_0	10.9	2.0038_9	12.5
2	20	2.0030_0	10.3	2.0038_2	13.1
3	35	2.0028_8	10.1	2.0033_3	14.3
4	75	2.0028_0	9.9	2.0030_9	14.8
5	100	2.0027_4	9.8	2.0030_9	14.8

[a] Microwave power = 0.6 mW.

obtained under various conditions, are summarized in Table 2.

We found that the compression of POEPA at room temperature resulted in a 4.8-fold increase in radical concentrations from 3.1 × 10^{16} spins/g at 0 kg/cm^2 to 1.55 × 10^{17} spins/g at 200 kg/cm^2. We further noticed that the g value observed before compression was rather large, $g = 2.0033_0$, and that compression shifted the g value to a higher magnetic field side, $g = 2.0027_4$, which is similar to that of nonsubstituted polyacetylene bearing $g = 2.0026$.[7,20] The change in the observed g value suggests that before the compression the magnetic interaction between radical spins stabilized in the cis chain and oxygen with a large spin orbit coupling constant in the EtO group exists[21] and after the compression the spin delocalizes in the trans sequence, as has been demonstrated for nonsubstituted *trans*-polyacetylene.[20,21] These results suggest that the ESR signals after the compression can be simulated as Lorentzian line shapes with line widths, $\Delta Hmsl = 12.5$ G ($g = 2.0027_4$), as shown in Figure 4f. These findings coincide, therefore, to the results cited above, i.e., the compression of the cis POEPA polymer bearing a less conjugated structure was transferred to a more conjugated polyacetylene structure; in other words, trans-transoid forms have planar trans zigzag sequences where unpaired electrons stabilized in the trans polymer chains can freely move around along the trans-conjugated chain as the trans-**Spin**-trans[20,22] called mobile unpaired electrons, i.e., solitons, as shown in Scheme 2. On the other hand, the pristine cis-transoid polymer does not possess such mobile unpaired electrons but, rather, has immobile unpaired electrons, because the cis electrons are stabilized in the restricted cis-transoid and/or cis-cisoid form as cis-**Spin**-trans and/or cis-**Spin**-cis radicals as shown in Scheme 2. Therefore, the mobile electrons stabilized in the trans-conjugated chain should show a motional narrowing in the line width of the ESR spectra as the case of poly((*o*-methoxyphenyl)-acetylene), POMPA,[10] and nonsubstituted polyacetylene.[20,22] A detailed investigation was carried out with respect to temperature dependence of the line width in the ESR spectra in order to determine if the radicals behave as mobile electrons. Figure 5 shows the temperature dependences of line width observed when the exerted pressure to the polymer was increased. It is clear that the largest increment in the line width from 9.8 to 14.8 G was induced when a pressure of 100 kg/cm^2 was exerted on the polymer although, before compression, the change in the line width is fairly small, i.e., from 10.9 to 12.5 G. This suggests that after the compression, a motional narrowing and/or exchange narrowing mechanism operates between the radical spins which is different from the case of the pristine polymer before the compression.[20,22,23]

Scheme 2



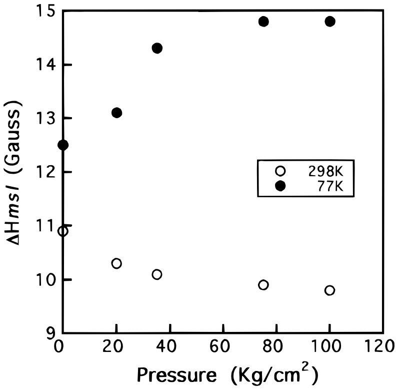
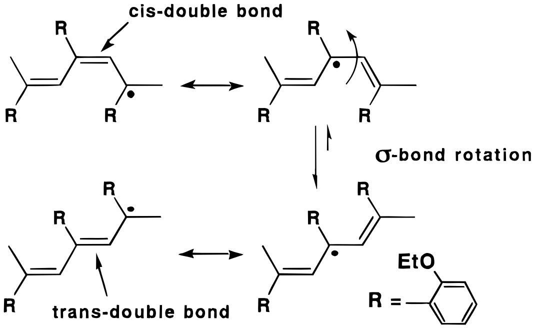


Figure 5. Temperature dependences of the line widths in the ESR spectra observed: (○) room temperature; (●) 77 K.

Table 2 shows temperature dependences of g values. It is seen that the g values are shifted to a lower magnetic field even in the pristine polymer when it is

Scheme 3



cooled from 300 to 77 K. This shift suggests that the spin glass or aggregation of the radical spins is generated even at room temperature. In other words, formation of an internal magnetic field due to inter- and/or intramolecular radical spins in the solid state takes place as has been deduced.[9a,24,25] Thus, the results obtained from UV, laser Raman, and ESR methods are in good agreement with one another.

The radicals which are stabilized in the pristine polymer are probably created by the isomerization of the cis polymer to the trans polymer through the rotational scission of the cis double bonds during the polymerization and/or by simply standing in solution.[6,19]

The pressure-induced cis−trans isomerization may be explained by a radical mechanism, since the radicals were detected both before and after compression. Obviously, the compression may enhance the isomerization to the more stable trans form through the rotational scission of the cis double bond in the cis polymers as shown in Scheme 3.

Therefore, the ortho-substituted polyacetylene with high cis content may function as the origin of the radical spins necessary for forming an organo-magnetic material, such as spin glass[24,25] 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 undergoes scission whose radicals aggregate each other as predicted in our previous report.[8,9a,24]

X-ray Diffraction. Wide-angle X-ray diffraction (WAXD) patterns of POEPA were recorded before and after compression. It seems that the POEPA polymer has a pseudohexagonal packing structure after compression as reported earlier for the cases of poly(ethynylcarvazole),[26] poly((*o*-methoxyphenyl)acetylene),[10] poly((*p*-methylphenyl)acetylene),[9b] poly(phenylacetylene),[9c] and poly(*n*-alkylpropiolate).[11] The WAXD patterns observed after compression at 75 kg/cm^2 showed diffraction peaks at $2\theta = 8.7°$ ($d = 10.16$ Å), $2\theta = 15.7°$ ($d = 5.65$ Å), and $2\theta = 22.2°$ ($d = 4.00$ Å). The 4.00 Å peak is broad and may be associated with noncrystalline components. The two sharp peaks are not suffiecient to deduce the exact packing of the molecules. The cis−transoid polymer sequence which was stereoregularly polymerized using a Rh complex catalyst appears to be rigid. On the other hand, the polymer chains which are associated with the radical spins do not appear to have linear chains in part, but, instead, bent structures, except for the fairly long conjugated trans−transoid chain sequences as shown in Schemes 2 and 3. In this case the polymer chains which involve radical spins may be gathered and expected to show magnetic dipole−dipole interactions between the gathered spins, although the magnetic interactions resulted in the increase of the line width of the ESR spectra and/or formation of spin glass as has been proposed by us.[9b,25] Thus, the physicochemical results with respect to the compressed POEPA polymer are in good agreement with each other.

Conclusion

We have succeeded in the stereoregular synthesis of the POEPA polymer with a helical chain in the presence of the Rh complex [Rh(NBD)Cl]$_2$ and have characterized the compressed POEPA where the conformational change, i.e., isomerization from cis to trans form was induced together with the generation of a number of radical spins which shows motional narrowing for the line width in the ESR spectra.

We are currently studying the magnetic properties of the compressed polymers using a SQUID magnetometer and whether aromatic polyacetylenes other than the POEPA polymer also can be produced by pressure-induced isomerization to generate potential useful trans-conjugated sequences bearing radical spins.

Acknowledgment. This work was supported in part by Grants-in-Aid for Scientific Research (Nos. 07246202 and 07455368) from the Ministry of Education, Science, and Culture, Japan.

References and Notes

(1) Tabata, M.; Yang, W.; Yokota, K. *Polym. J.* **1990**, *22*, 1105.
(2) Yang, W.; Tabata, M.; Yokota, K.; Shimizu, A. *Polym. J.* **1991**, *23*, 1135.
(3) Tabata, M.; Inaba, Y.; Yokota, K.; Nozaki, Y. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 465.
(4) Tabata, M.; Yang, W.; Yokota, K. *J. Polym. Sci., Polym. Chem. Ed.* **1994**, *32*, 1113.
(5) Minakawa, H.; Tabata, M.; Yokota, K. *J. Macromol. Sci., Pure Appl. Chem.* **1996**, *A33*, 291.
(6) Lindgren, M.; Lee, H.-S.; Yang, W.; Tabata, M.; Yokota, K. *Polymer* **1991**, *32*, 1532.
(7) Tabata, M.; Yokota, K.; Namioka, M. *Macromol. Chem. and Phys.* **1995**, *196*, 2969.
(8) Tabata, M.; Yokota, K.; Namioka, M. *Polymer* **1996**, *37*, 1959.
(9) (a) Tabata, M.; Nozaki, Y.; Yang, W.; Yokota, K.; Tazuke, Y. *Proc. Jpn. Acad.* **1995**, *71B*, 219. (b) Tabata, M.; Kobayashi, S.; Sadahiro, Y.; Yokota, K. *J. Macromol. Sci., Pure Appl. Chem.* **1997**, *A34*, 505. (c) Tabata, M.; Sadahiro, Y.; Yokota, K.; Kobayashi, S. *Jpn. J. Appl. Phys.* **1996**, *35*, 5411. (d) Unger, G. *Polymer* **1993**, *34*, 2050.
(10) Tabata, M.; Takamura, H.; Yokota, K.; Nozaki, Y.; Hoshina, T.; Minakawa, H.; Kodaira, K. *Macromolecules* **1994**, *27*, 6234.
(11) Tabata, M. ; Sadahiro, Y.; Nozaki, Y.; Inaba, Y.; Yokota, K. *Macromolecules* **1996**, *29*, 6673.
(12) Masuda, T.; Higashimura, T. *Adv. Polym. Sci.* **1986**, *81*, 121.
(13) Korshak, Y. V.; Medvedeva, T. V.; Ovchinnikov, A. A.; Spector, V. *Nature* **1987**, *32*, 370.
(14) Neher, D.; Wolf, A.; Bubeck, C.; Wegner, G. *Chem. Phys. Lett.* **1989**, *163*, 116.
(15) Lefrant, S.; Lichtman, L. S.; Temkin, H.; Fitchen, D. B.; Miller, D. C.; Whitwell, G. E.; Burlitch, J. M. *Solid. State. Commun.* **1979**, *29*, 191.
(16) Tabata, M.; Nozaki, Y.; Yokota, K. *J. Photopolym. Sci., Technol.* **1993**, *6*, 1.
(17) Harada, T.; Tasumi, M.; Shirakawa, H. *Chem. Lett.* **1978**, 1411.
(18) Masuda, T.; Hamano, K.; Tsuchihara, K.; Higashimura, T. *Macromolecules* **1990**, *23*, 1374.
(19) Kunzler, J.; Percec, V. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 1221 and references cited therein.
(20) Shirakawa, H.; Ito, T.; Ikeda, S. *Makromol. Chem.* **1978**, *179*, 1565.
(21) Tabata, M.; Lund, A. *Chem. Phys.* **1983**, *75*, 379.
(22) Goldberg, I. B.; Crowe, P. R.; Newman, P. R.; Heeger, A. J.; MacDiarmid, A. G. *J. Chem. Phys.* **1979**, *70*, 1132.
(23) Tomkiewicz, Y.; Schultz, T. D.; Broom, H. B.; Clarke, T. C.; Street, G. B. *Phys. Rev. Lett.* **1979**, *43*, 1532.
(24) Tabata, M. *Adv. Mater.* (in Japanese) **1991**, *11*, 44.
(25) Nagata, K. *J. Phys. Chem., Jpn.* **1976**, *49*, 1209.
(26) Griffiths, C. H. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1167.

MA960766C