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Generation of polyacetylene sulfoxide radicals through spin migration from the main-chain to the sulfoxide moiety in the side chain of poly[*p*-(*n*-butylsulfoxide)phenylacetylene] prepared with a [Rh(norbornadiene)Cl]$_2$ catalyst

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Abstract

A phenylacetylene bearing an *n*-butylsulfoxide group, i.e., *p*-(*n*-butylsulfoxide)phenylacetylene (**1**) was prepared in high yields using the [Rh(norbornadiene)Cl]$_2$–NEt$_3$ catalyst in the presence of various solvents under mild conditions. The resulting polymer, poly[*p*-(*n*-butylsulfoxide)phenylacetylene] (poly(**1**)), was characterized in detail by ^{1}H NMR, ESR, laser Raman, and diffuse reflective UV–vis methods. The data clearly showed that *cis*-to-*trans* isomerization of the polymer can be induced when pressure is imposed to the polymer at room temperature, rotationally breaking the *cis* C=C bonds to generate the *cis* and *trans* radicals. Further, the spin density in the *cis* radical was migrated from the main-chain to the sulfoxide moiety as the side chain of the phenyl ring to magnetically interact with the first two methylene protons in the *n*-butyl group giving a triplet line ESR spectrum with an extremely large *g* value, $g = 2.0081$.
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Keywords: Sulfoxide radical; *cis*-to-*trans* isomerization; Polyacetylene

1. Introduction

Polymerization of phenylacetylene (PA) and its derivatives has been well studied, and the resulting poly(phenylacetylene)s (PPAs) have been found to exhibit novel physicochemical properties such as conductivity [1,2], photoconductivity [3,4], liquid crystallinity [5–7], light emission [8,9], gas and liquid permselectivity [10], third-order nonlinear susceptibility [11], spin glass [12,13], and chirality [14,15]. The geometrical structure of the aromatic polyacetylenes with high-*cis* content as well as control of the *cis* content is also essentially needed in order to unequivocally understand the physicochemical properties.

In our previous reports [16–21], we have demonstrated that PA and its homologues can be stereospecifically polymerized in the presence of a Rh complex catalyst: [Rh(nbd)Cl]$_2$, (nbd = norbornadiene), to selectively give the *cis*–*transoid* isomer having an helical structure in high yields under quite mild conditions when triethylamine (NEt$_3$) or an alcohol is used as the polymerization solvent. In addition, the PPA derivatives prepared with the Rh complex can be easily isomerized from the *cis* form to the *trans* form, when the *cis*-polymer powder is subjected to compression at room temperature under reduced pressure [22,23], although the *cis*-to-*trans* isomerization of such aromatic polyacetylenes can be induced by thermal treatment [24–26], γ-irradiation [27], and photo-illumination [28].

In this report, we newly show that poly[*p*-(*n*-butylsulfoxide)-phenylacetylene] (poly(**1**)) can be successfully prepared in high yields using the Rh complex catalyst (Scheme 1)

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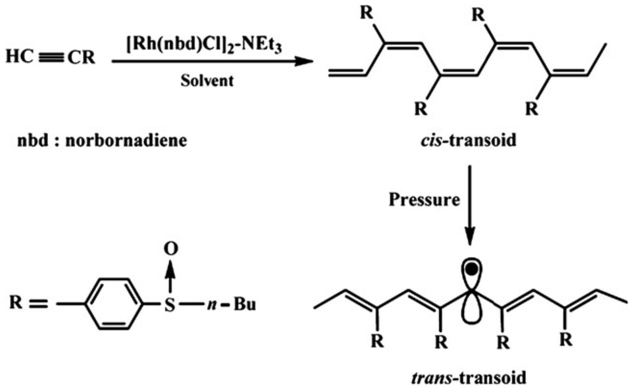


Scheme 1. Synthesis of polyacetylene having *cis* form and pressure induced *cis*-to-*trans* isomerization.

without any deactivation of the Rh complex catalyst by such sulfoxide moiety in the monomer. This monomer having alkyl sulfoxide moiety with the Lewis base property has never been polymerized with not only the rhodium catalyst but also the Ziegler–Natta catalyst. Further, formation of a novel polyacetylene sulfoxide radical through the pressure-induced *cis*-to-*trans* isomerization is also reported together with the detailed characterization of the polymers using ^{1}H NMR, laser Raman, diffuse reflective UV–vis (DRUV–vis), and electron spin resonance (ESR) methods.

It may be expected that helical polyacetylene having the alkyl sulfoxide moiety as the side chain of the phenyl ring plays an important role, i.e., the sulfoxide moiety reacts with gold surface which may be a new technique connecting with sulfoxide polymer and gold metal surface suggesting appearance of a new comer as an electronic device other than usual alkyl thiol function.

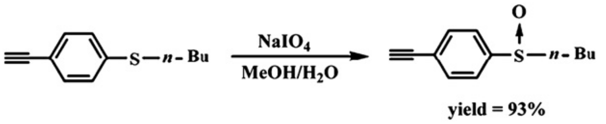
2. Experimental section

2.1. Materials

The starting material, *p*-(*n*-butylthio)phenylacetylene, was prepared by the reported method [29]. Sodium metaperiodate was purchased from Junsei Chemical Co., Ltd. The Rh complex catalyst $[Rh(nbd)Cl]_2$ (Aldrich Chemical Co.) was used without any further purification. Polymerization solvents: toluene, NEt_3, and $CHCl_3$, were purified and dried before use according to conventional methods.

2.2. Synthesis of p-(n-butylsulfoxide)phenylacetylene (1)

The sulfoxide monomer, **1**, was synthesized according to an equation shown in Scheme 2. To a mixture of sodium metaperiodate (2.95 g, 13.8 mmol) and distilled water (13 ml) at 0 °C were added *p*-(*n*-butylthio)phenylacetylene (2.17 g, 13.2 mmol) and methanol (50 ml). The mixture was stirred at ice-bath temperature for 24 h. The reaction mixture was extracted with $CHCl_3$ and the organic layer was dried over anhydrous magnesium sulfate. After the solvent was removed, the crude product was purified by column chromatography (silica gel, $CHCl_3$) to give *p*BuSOPA (2.5 g, 93%) as a pale yellow solid.



Scheme 2. Synthesis of *p*BuSOPA.

2.3. Polymerization

Poly(**1**) was obtained by the polymerization of **1** under various conditions. In a typical procedure, 2×10^{-3} mol of **1** and the calculated amount of the catalyst were dissolved in the solvent separately using a specially designed U-shaped ampoule [19] in our laboratory. The solution was mixed and stirred according to the time and temperature reported in Table 1. The reaction mixture was poured into excess amount of methanol to precipitate a polymer. The resulting polymer was washed with methanol and dried under dynamic vacuum, ca. 10^{-2} mmHg for 24 h. The yields with number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) are reported in Table 1. Elemental analysis: $(C_{12}H_{14}SO)_n$ $(190.3)_n$: calcd. C 75.74, H 7.42, S 16.85; found C 74.96, H 7.17, S 16.18.

2.4. Measurements

Polymers were compressed at 200 kg/cm^2 for 10 min under dynamic vacuum, ca. 10^{-2} mmHg at room temperature using an oil press for manufacturing a KBr disk. The ^{1}H NMR spectra of the polymers were recorded on a JEOL JNM-A400 MHz spectrometer at room temperature using $CDCl_3$. Gel permeation chromatographic (GPC) measurements were performed with a JASCO GPC 900-1 chromatograph with an RI detector using two Shodex K-806 L columns, $CHCl_3$ as an eluent and polystyrene as a standard. DRUV–vis spectra of the polymers before and after compression were recorded on a JASCO V-570 spectrophotometer equipped with an ISN-470 integrating sphere accessory. Samples were mixed with 200 mg of alumina and 3 mg of the solid polymer. Laser Raman spectra were observed on a JASCO TRS-401 spectrometer equipped with triple monochromators using Ar^+ laser light at 514.5 nm after mixing of polymer 3 mg and KBr 200 mg. ESR spectra were obtained using a JEOL FE1XG spectrometer with 100 kHz modulation

Table 1
Polymerization of **1** by $[Rh(nbd)Cl]_2$ catalyst[a]

No.	Monomer	Solvent	Temp. (°C)	Yield (%)	M_n[c]	M_w/M_n[c]
1	**1**	Toluene[b]	10	92	53,800	2.6
2	**1**	NEt_3	15	51	42,600	9.9
3	**1**	$CHCl_3$[b]	25	87	–[d]	–[d]

[a] Polymerization conditions: [cat.]/[M] = 1/100; 2 h.

[b] NEt_3 was used as the co-catalyst, [co-cat.]/[cat.] = 100.

[c] Measured by GPC using $CHCl_3$ as eluent and using polystyrene as a standard.

[d] Insoluble in $CHCl_3$.

at room temperature. Semi-empirical quantum calculation of spin density together with polymer structures was performed using Spartan MMFF94 force field (Wavefunction, Inc., Spartan '04 Windows version 1.03).

3. Results and discussion

3.1. Polymerization

The monomer **1** was polymerized using the Rh complex catalyst in various solvents to determine the best conditions for polymerization. The polymerization results are shown in Table 1. It is clear that the polymers were obtained in fairly high yields even within 2 h at 10–25 °C when chloroform or toluene solution involving NEt_3 as the co-catalyst was used. The obtained polymers were soluble in $CHCl_3$, toluene, and THF, and insoluble in methanol, ethanol, NEt_3, and water. In contrast, unlike the previous cases, the polymer was obtained in relatively low yield and large M_w/M_n when neat NEt_3 was used as the polymerization solvent [16–21].

3.2. ^1H NMR spectra

Fig. 1a shows the ^1H NMR spectrum of poly(**1**) (No. 1 in Table 1), which was measured in order to determine the *cis–transoid* content of the polymer using $CDCl_3$ at room temperature. Peaks observed at 0.88 ppm (3H), 1.35 ppm (2H), 1.73 ppm (2H), 2.67 ppm (2H), 5.78 ppm (1H), 6.80 ppm (2H), and 7.26 ppm (2H), can be assigned to the $-CH_3$, $-CH_2CH_3$, $-CH_2CH_2CH_3$, $-SOCH_2-$, $=CH$ (main-chain), and CH (phenyl) protons in the polymer, respectively.

The *cis* ratio was estimated as ca. 91% using the integral intensity ratio, i.e., 0.91/2.0 between the main-chain $=CH$ proton and the $-SOCH_2-$ proton. In addition, the narrow line-width observed in the ^1H NMR spectrum may reflect no irregular sequences such as a head-to-head and/or tail-to-tail structure, or a cyclohexadienyl moiety as a result of intramolecular cyclization [30,31]. Fig. 1b and c shows the expanded ^1H NMR spectra in the chemical shifts region due to $-SOCH_2-$ protons before and after compression of poly(**1**), respectively, although the whole spectrum having broader line widths observed after compression is not shown in those spectra. We found that each line-width is increased by the compression to some extent compared with that of the pristine polymer as shown in Fig. 1a. This suggests that compression of the polymer effects the *cis*-to-*trans* isomerization to produce *trans* π-conjugated sequences which can stabilize unpaired electrons as mobile electrons called solitons as discussed below [18,21,23,29,32]. The compression can break the *cis* C=C double bonds rotationally in order to create two unpaired electrons as biradicals which may be diffused as the π-radicals called solitons along the resulting π-conjugated planar main-chain [32]. The resulting *cis* and *trans* radicals having a magnetic spin, $S = 1/2$, may increase the line-width of the ^1H NMR spectrum through the so-called magnetic dipole–dipole (D–D) interaction between magnetic spins and protons in the polymer [21,33].

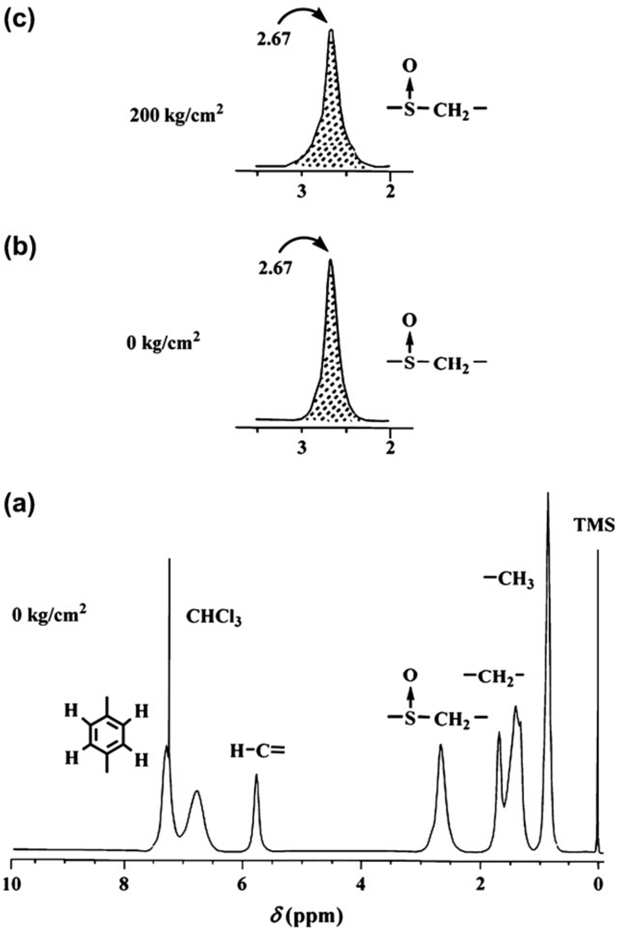


Fig. 1. ^1H NMR spectra of poly(**1**) (No. 1 in Table 1) observed in chloroform-d_1 solution at room temperature. (a) Full scale spectrum of poly(**1**), (b) expanded peak of $-SOCH_2-$ protons before compression, and (c) expanded peak of $-SOCH_2-$ protons after compression at 200 kg/cm^2 under reduced pressure at room temperature.

The ratio of the *trans* sequences generated by compression was estimated as ca. 18% by comparing the areas of the $=CH$ proton peak with that of the $-SOCH_2$ proton peak in the ^1H NMR spectrum [21,33]. This isomerization will be also proven by the Raman and ESR data observed after the compression as mentioned below.

3.3. Planar *trans* π-conjugated sequence generated by compression

3.3.1. Laser Raman spectra

The laser Raman spectra of poly(**1**) (No. 1 in Table 1) observed before and after the compression are shown in Fig. 2.

After compression, new peaks clearly appeared at 1210 cm^{-1} and 1480 cm^{-1}. The latter peak at 1480 cm^{-1} was assigned to a *trans* C=C bond in the newly created planar *trans* π-conjugated sequences [32,33]. The conjugation length was estimated to be $n = 24$ for 1480 cm^{-1} in the $(C{=}C)_n$, using the so-called Shirakawa–Tabata (ST) relationship [22,33,34] where a relationship between the laser Raman peak and the number of the C=C bond in the *trans* polyenes, $(C{=}C)_n$, is

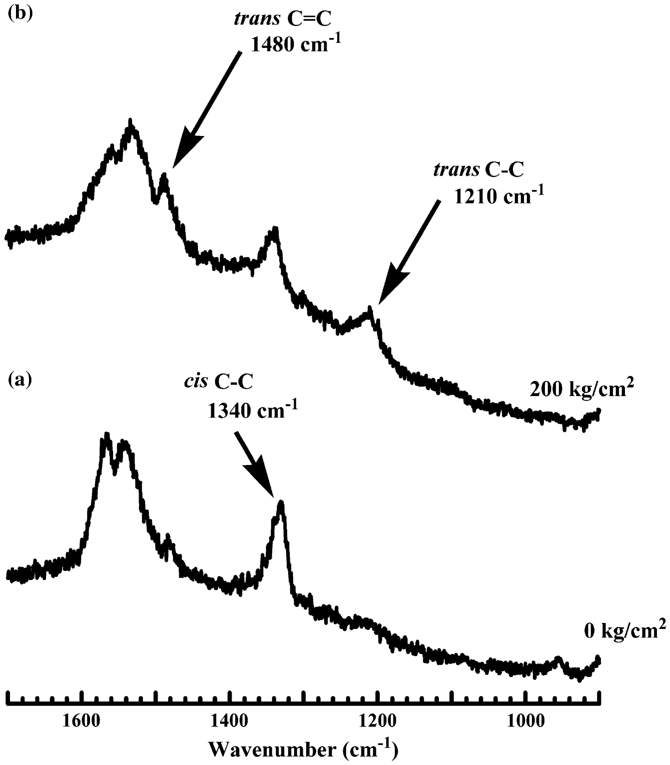


Fig. 2. Laser Raman spectra of poly(**1**) (No. 1 in Table 1) observed at room temperature. (a) Before and (b) after compression at 200 kg/cm^2 under vacuum at room temperature.

depicted. Thus, it is clearly concluded that poly(**1**) can also be isomerized by compression to incorporate fairly long *trans* π-conjugated sequences in the pristine *cis* sequences at room temperature. The driving force of the pressure-induced *cis*-to-*trans* isomerization may be ascribed to the difference in the effective molecular volumes between the *cis* isomer and the *trans* isomers, i.e., the molecular volume of the *trans* isomer is approximately one-half compared with that of the *cis* isomer as expressed below in Eq. (1) (Scheme 1).

$$\text{Volume of } cis \text{ isomer} \approx 2 \text{ volume of } trans \text{ isomer} \tag{1}$$

3.3.2. DRUV–vis spectra

DRUV–vis spectra of poly(**1**) (No. 1 in Table 1) were used to determine the conjugation lengths of the polymers observed before and after compression as shown in Fig. 3. After compression, the absorption maximum was shifted to a longer wavelength side, i.e., from 450 nm for the pristine polymer to 470 nm associated with decrease of the absorption intensity. The difference spectrum obtained by subtraction of the absorption spectra observed before and after compression at room temperature is shown in Fig. 3c where a new absorption maximum is depicted at a fairly longer wavelength, i.e., 550 nm. The new absorption band can be attributed to that of the fairly long *trans* π-conjugated sequences created by compression. The relationship between n in *trans* polyenes, (C=C)n, and the UV–vis absorption peak is also estimated as $n = 27$ by using the ST relationship [22,33,35]. Thus, the *trans* conjugation length estimated from the Raman and DRUV–vis data which was observed after the compression mostly agreed with each other.

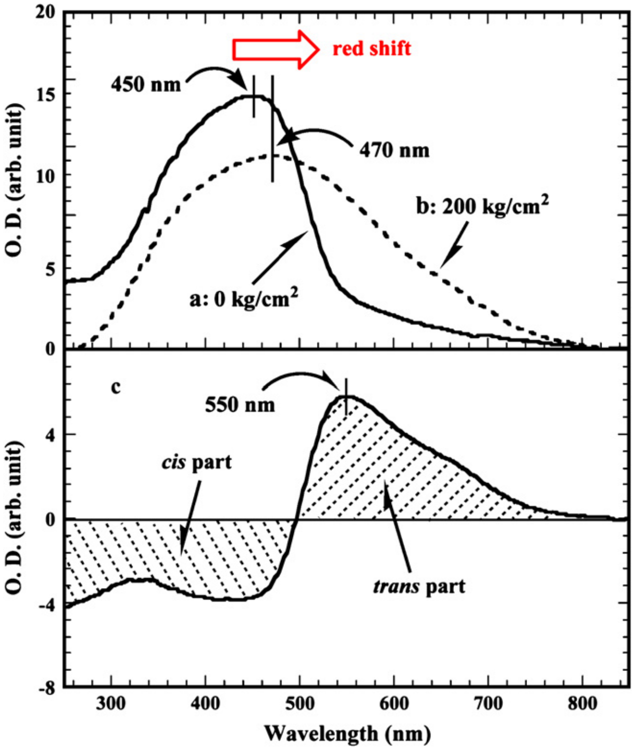


Fig. 3. Diffuse reflective UV–vis spectra of poly(**1**) (No. 1 in Table 1) observed at room temperature. (a) Before and (b) after compression at 200 kg/cm^2 under vacuum at room temperature, and (c) the subtraction spectrum.

3.4. ESR spectra

Previously, we reported [18,21,29,33] that the g value of not only aromatic but also aliphatic polyacetylenes such as poly(alkylpropiolate)s can be used to deduce the geometrical structures, i.e., *cis* form or *trans* form, when one hetero atom such as an O or N is substituted within the side chain of the polyacetylene molecules. Such a hetero atom has a relatively large spin orbit coupling constant, ζ [36,37], compared with that of the hydrocarbon radicals. We also revealed [18,22,23] that the hetero atom can induce the g value shift to a lower magnetic field, especially in the *cis* form, although in the case of the *trans* form such a shift 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 the planar *trans* π-conjugation plane are nearly perpendicular to each other where such strong magnetic interaction is not decoupled between the hetero atom in the side chain and the unpaired electrons in the main-chain.

The ESR spectra of poly(**1**) (No. 1 in Table 1) observed before and after compression are shown in Fig. 4. The microwave power saturation effect [38] in the ESR spectrum of poly(**1**) was examined in order to determine whether this polymer is composed of two chemical species ascribable to the *cis* radical and *trans* radical. It is clear that the line shape changes

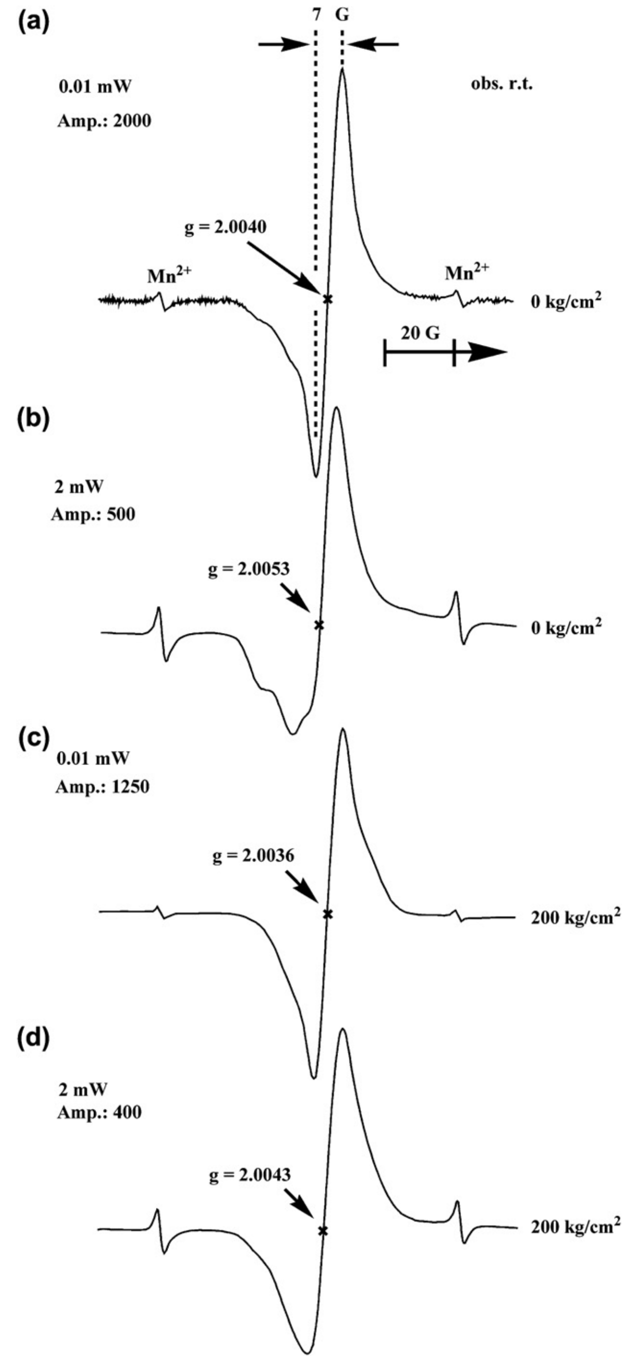


Fig. 4. Microwave power saturation effect on the ESR spectra of poly(**1**) (No. 1 in Table 1) observed at room temperature and microwave power at (a and c) 0.01 mW and (b and d) 2 mW.

were induced with increasing microwave power from 0.01 mW to 2 mW. This suggests that the observed ESR spectra are composed of at least two radicals, i.e., the *cis* and *trans* radicals, which were created by rotational scission of the *cis* C═C bonds in this polymer. The sharp and symmetrical line shape spectrum having line-width, $\Delta H_{\mathrm{msl}} = 7.1$ G and g value = 2.0040 was observed when the pristine poly(**1**) was subjected to low microwave power of 0.01 mW (see Fig. 4a). This spectrum may be assigned to that of the *trans* radical due to fairly small g value. This spectrum was simulated in order to deduce the *trans* radical's spectral parameters, i.e., g value and line-width assuming the so-called Lorentzian line shape [22,23,32]. In contrast, at a higher microwave power, 2 mW, the spectrum became unsymmetrical and the g value was increased from 2.0040 to ca. 2.0053 (see Fig. 4b). Thus, this spectrum is composed of the *cis* and *trans* radicals. Further, this shows that microwave power saturation technique is very useful for the detection method of the two radicals even at room temperature.

This saturation effect was also applied to the compressed polymer in order to distinguish the *cis* radical and *trans* radical spectral components in the polymer. The results are shown in Fig. 4c and d. We found that even after compression a sharp spectrum bearing the Lorentzian line shape can be observed at 0.01 mW, and a fairly broad spectrum was also observed at 2 mW. Thus, the *cis* and *trans* radicals can be easily distinguished by using the microwave saturation effect, because the *cis* and *trans* radicals have completely different line shapes together with different microwave saturation effects, although the sharp line spectral component due to the *trans* radical is easily saturated at such higher power, 2 mW. The radical spin concentrations before and after compression were estimated as 6.3×10^{17} spins/g and 8.5×10^{17} spins/g, respectively.

We found that in the second derivative ESR spectra (Fig. 5) of poly(**1**) observed even before compression a very larger g value, 2.0081 due to the *cis* radical, and small g value, 2.0038 due to *trans* radical, can be separately observed. These observed g values completely agreed with the simulated spectra shown below. It seems that, to the best of our knowledge, the *cis* radical holding such an extremely large g value has never been reported up to date in the polyacetylenes. This result is quite important because such a large g value was not deduced from the spin orbit coupling constant, $\zeta = 382\ \mathrm{cm}^{-1}$ [36,37], of the sulfur atom itself.

Computer simulation [39] was performed to deduce the spectral components, assuming that the triplet and singlet spectra assigned to the *cis* and *trans* radicals, respectively, bearing different g values are superimposed to each other as shown in Fig. 5b. The simulated spectrum is shown in Fig. 5e, where $g = 2.0081$ and line-width: $\Delta H_{\mathrm{msl}} = 11$ G are assumed for the triplet of the *cis* isomer radical (see Fig. 5c), and $g = 2.0038$ and line-width $\Delta H_{\mathrm{msl}} = 7$ G are assumed for the singlet of the *trans* isomer radical (see Fig. 5d), although the planar *trans* conjugated radical may be created by the repeated bond rotation marked with α bond in Scheme 3. The singlet line simulated with the so-called Lorentzian line shape suggests that the resulting *trans* isomer radical has planar *trans* zigzag conjugated sequences similar to Shirakawa's polyacetylene [40]. It is noteworthy that the spectral component bearing the Lorentzian line shape due to the *trans* radical was easily suppressed when high microwave power was imposed to the compressed polymer (see Fig. 4) as reported before [29]. This may mean that the resulting *trans* sequences have fairly planar configuration which can stabilize the π-radical as a mobile unpaired electron similar to the so-called soliton as studied by Shirakawa and Heeger's group and so on [22,23,34,35,40]. On the

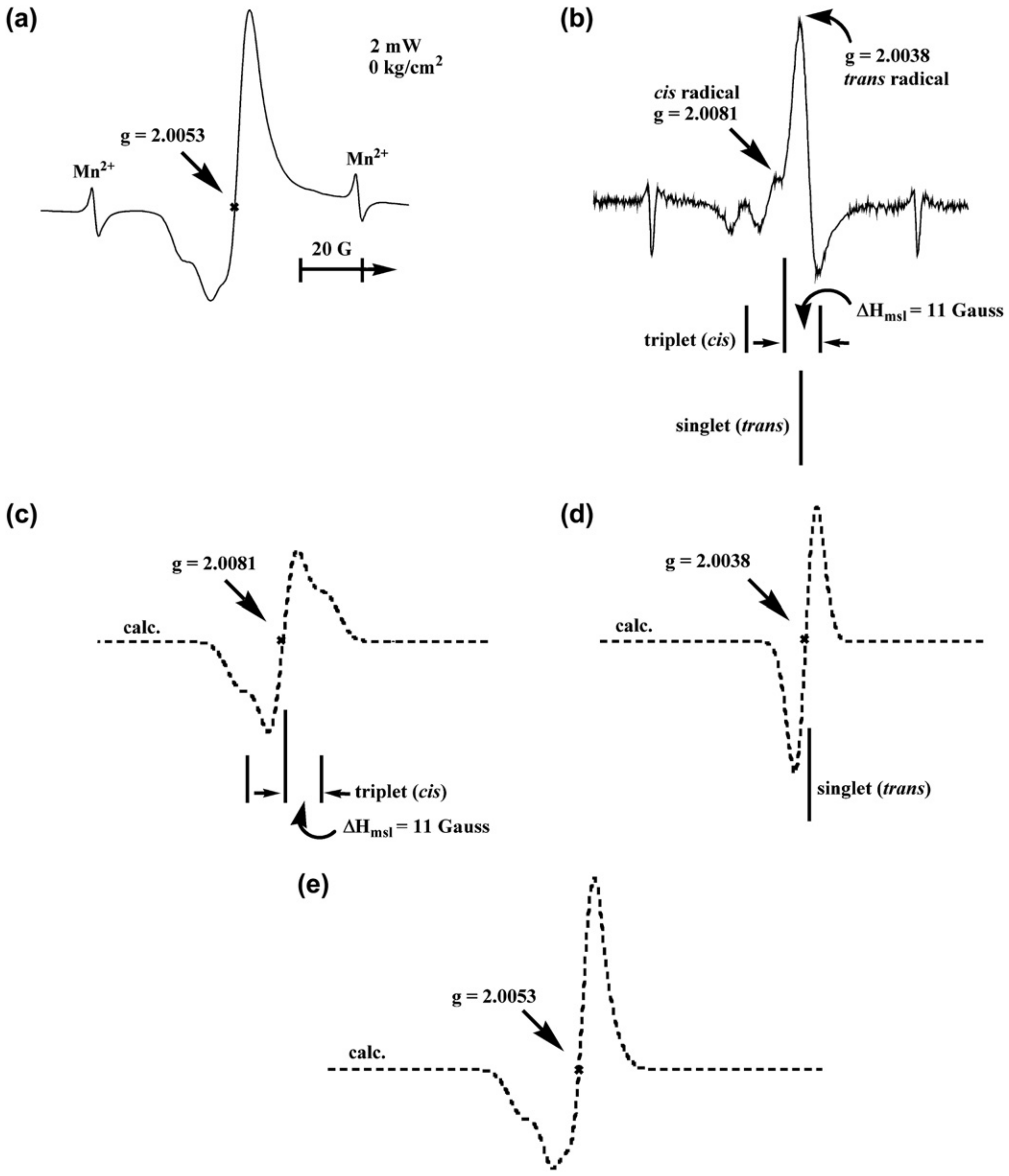
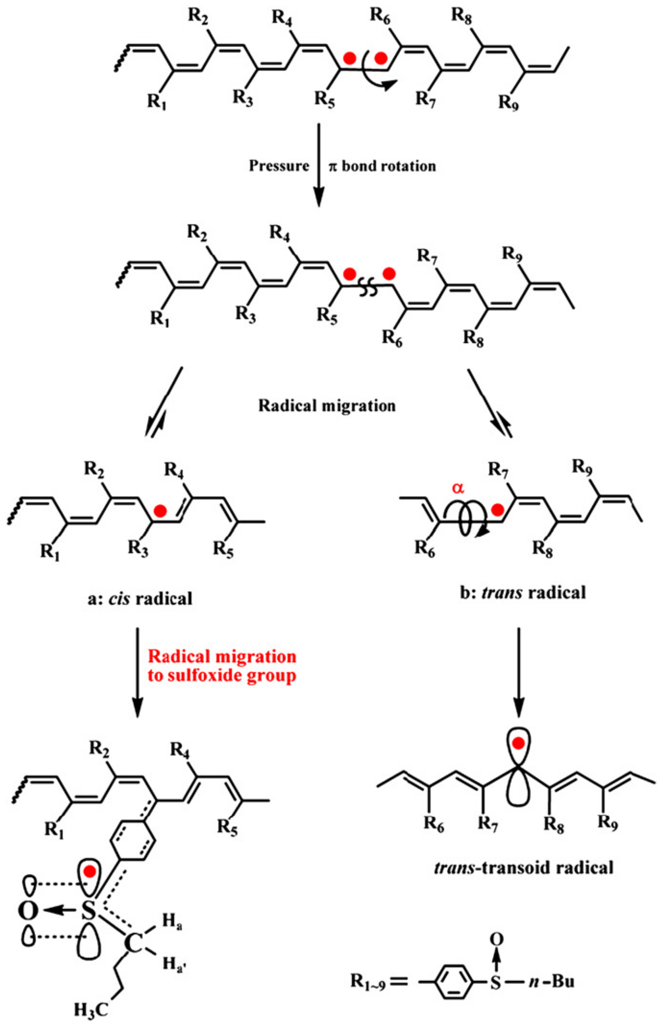


Fig. 5. The ESR spectra of poly(**1**) (No. 1 in Table 1) observed at room temperature (a) before compression, (b) second derivative ESR spectra, (c) simulated *cis* radical spectrum, (d) simulated *trans* radical spectrum, and (e) simulated spectrum.

other hand, the observed triplet can be ascribed to that of the *cis* radical where the unpaired electron is fairly localized at not the main-chain but the sulfoxide moiety in the side chain of the phenyl group as discussed below.

3.5. Semi-empirical quantum chemical calculation

Conformational analysis using the AM1 program [41] was performed for poly(**1**) to determine the most energetically stable conformation of their isomers and distribution of the unpaired electrons produced by the rotational scission of the pristine *cis* C═C bond during not only polymerization but also by compression of the polymer. A quinoid structure (see Fig. 6a) as the model structure of the *cis* radical moiety was assumed to calculate where the spin density is localized or delocalized in the pristine polymer. In this quinoid structure, the AM1 calculation clearly showed that the sulfur orbit was taken as sp^2 configuration and the spin density was localized not only on the sulfur atom but also on the two alkyl protons nearest the sulfur atom. However, the two double bonds in the model structure were needed to configurate a typical coplanar as shown in Fig. 6a. Thus, the migration of the unpaired electrons, which were generated by the rotational scission of the *cis* C═C double bonds in the main-chain when compressed, resulted in generation of a new sulfoxide radical, and the ratio of the spin density was calculated as 15/1.0 in the sulfur and oxygen atoms. Therefore, we can successfully explain the reason why the *g* value observed in poly(**1**) is extremely large, 2.0081, because the very large spin density can be localized on the sulfur atom which has also such a large orbit coupling constant $\zeta = 382$ giving a novel sulfoxide radical, although the spin orbit coupling constant is unknown as the moiety up to date.



Scheme 3. Possible pressure-induced *cis*-to-*trans* isomerization through the *cis* double bond rotation.

The singlet line may be attributed to the *trans* radical stabilized in the conjugated main-chain, because the resulting *trans* sequences have fairly planar configuration which can stabilize the π-radical as a mobile unpaired electron similar to the so-called soliton where seven main-chain protons may be magnetically coupled as proposed in Fig. 6b. Thus, the AM1 calculation reasonably explains our experimental results. The aromatic acetylenes having a large amount of the spin density at the end of the side chain may show an interesting magnetic behavior like the so-called spin glass as a novel time memory [12,13] and also magnetic materials for a useful radical cell.

4. Conclusion

The stereospecific polymerization of *p*-(*n*-butylsulfoxide)-phenylacetylene (*p*BuSOPA) was successfully performed using the Rh complex, $[Rh(nbd)Cl]_2$, catalyst in the presence of various solvents at room temperature to selectively produce the corresponding *cis–transoid* polymers in high yields. The compression of the resulting polymers at around 200 kg/cm^2 induced the *cis*-to-*trans* isomerization, as evidenced by the appearance of a new absorption band at a fairly longer wavelength in the diffuse reflective UV–vis spectra where the *trans* sequence having fairly long *trans* double bonds, $(C{=}C)_n$, $n = 27$, was generated. Additionally, the ESR spectrum of the polymers is composed of the *cis* and *trans* radicals. Further, the large *g* value, 2.0081 in the *cis* radical can be reasonably explained by the fact that the unpaired electron created by the rotational scission of the *cis* C=C bond can migrate on the alkyl sulfoxide moiety in order to magnetically couple with the two nearest methylene protons. The ratio of the spin density for the sulfoxide radical was calculated as 15/1.0 in the sulfur and oxygen atoms.

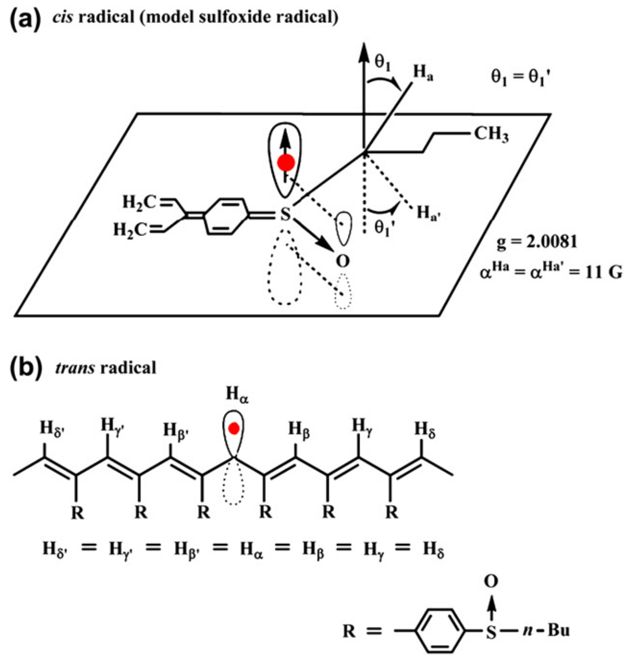


Fig. 6. (a) Proposed model structures for *cis* radical on the sulfoxide moiety and (b) *trans–transoid* radical structure.

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