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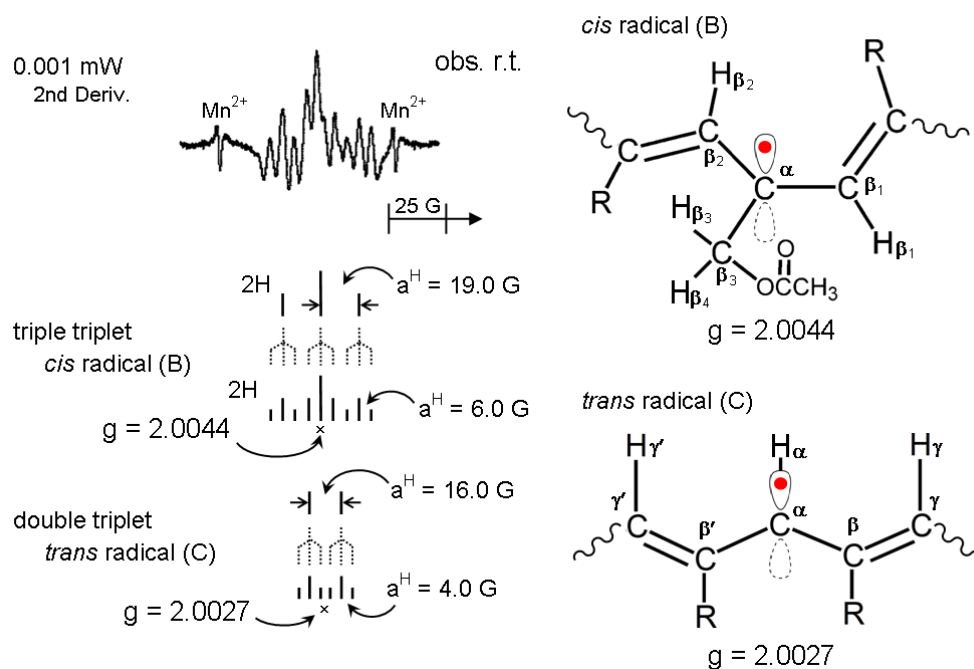
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ESR spectrum and radical structures



Graphical abstract

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Cis and *trans* radicals generated in helical poly(propargyl acetate)s prepared using a
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Abstract

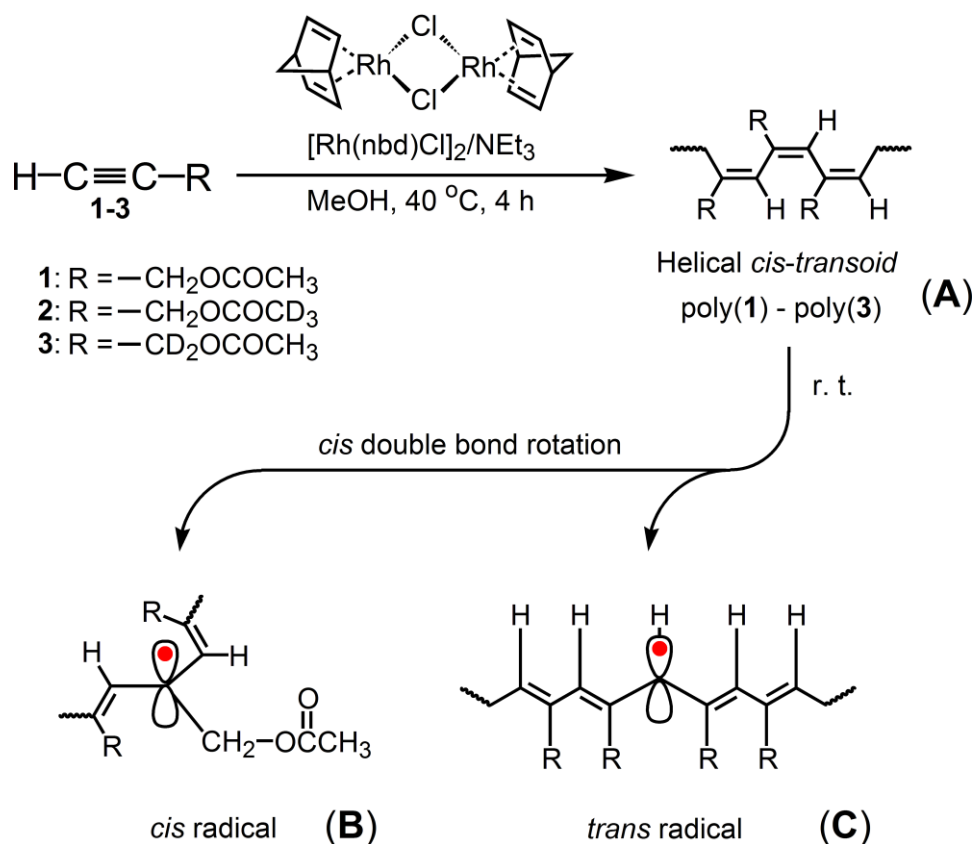
The poly(propargyl acetate) (**A**) having a helical *cis-transoid* structure was stereospecifically prepared using the Rh complex catalyst, [Rh(norbornadiene)Cl]₂, in MeOH or NEt₃ solvent at room temperature in moderated yield. Electron spin resonance (ESR) analysis of the polymer revealed the formation of the *cis* (**B**) and *trans* (**C**)

radicals which were produced through the thermal rotational scission of the helical *cis* C=C bonds in the main-chain during the polymerization. The spatial and geometrical structure was successfully deduced using the two analogues polymers in which either methyl or methylene group is deuterated, by the aide of computer simulation of the observed ESR spectra together with the calculation of spin density of the two radicals.

1. Introduction

Substituted polyacetylenes (SPs) have been considered as the typical conjugated polymers, which have interesting properties, e.g., pressure induced *cis*-to-*trans* isomerization [1], helix and columnar formations [2], molecular recognition ability [3-7], and non-linear optical (NLO) [8-9] and anti ferromagnetic (AFM) properties due to the *cis* and/or *trans* radical spins generated in the polymers [10-11]. The AFM properties are potentially important for a new type of time memory materials similar to human's neuron system [12]. The AFM property of the polymers was increased at the lower temperature, e.g., 58 K~114 K and in the prolonged time when the polymer was kept without magnetic field at a low temperature and finally the magnetization was saturated [13]. It was reported that poly(propargyl ester)s (PPE)s has humidity sensitive properties among the conjugated polymers which can be prepared by using Mo, W, Pd transition metal catalysts [14]. Recently, the polymerization of propargyl ester (PE) by using the so-called Zwitter ionic Rh catalyst in tetrahydrofuran, THF, was reported by Masuda and Noyori [15]. This catalyst is inactive in MeOH because of its deactivation

in alcoholic solvent. In the present report using a monodentate Rh catalyst: $[\text{Rh}(\text{nbd})\text{Cl}]_2/\text{NEt}_3$, (nbd = norbornadiene), we describe the polymerization of PE in MeOH. Radical species involved in the resultant *cis-transoid* poly(propargyl acetate)s (PPA)s were analyzed by Electron spin resonance (ESR) method and a spatial geometrical structure of the *cis* and *trans* radicals could be successfully determined. Both radicals (**B** and **C**) were produced through rotational scission of the *cis* C=C bonds of the *cis-transoid* polymer (**A**) by thermally induced *cis*-to-*trans* isomerization during the polymerization and/or on standing the polymer solution at room temperature [1d] not by the so-called pressure induced *cis*-to-*trans* isomerization [1a,b,c] (see Scheme 1).



Scheme 1.

2. Experimental section

2.1 Measurements

Number and weight average molecular weights (M_n and M_w) of polymers were measured using JASCO GPC 900-1 equipped with two Shodex K-806L columns and RI detector. Chloroform was used as an eluent at 40 °C and poly(styrene) standards ($M_n = 800$ – $1,090,000$) were employed for calibration. ^1H NMR and ^{13}C NMR spectra were measured on a JEOL JNM-EX270 and Bruker DSX-300 using chloroform-*d* as a solvent at room temperature. ESR spectra were recorded on a JEOL FE3XG (9.44 GHz) with 100 kHz field modulation at room temperature. A signal due to Mn^{2+} bedded in MgO was used for calibration of the magnetic field. In order to observe detailed information for the hyperfine coupling constant of the ESR spectra the second derivative spectra were measured at room temperature using lower microwave power. The energetically optimal conformation of PPA together with its spin density in order to explain the ESR spectral data was deduced from the ESR spectra by using semi empirical quantum chemical calculation AM1 method [16]. Computer simulation of the observed ESR spectra was performed using our own program [17].

2.2 Materials

2.2.1 Synthesis of propargyl acetate (**1**)

To a stirring mixture of 15.1 g (0.27 mol) of propargyl alcohol (TCI), 30.4 g (0.38 mol) of pyridine (KANTO) and 3.3 g (0.03 mol) of 4-(*N,N*-dimethylamino)pyridine (Aldrich) in 288 mL of dichloromethane (DCM), a solution of 25 g (0.32 mol) of acetyl chloride (KANTO) in 32 mL of DCM was added dropwise at 0-5 °C. After stirring for 24 h at room temperature, the resulting mixture was washed with a 5% HCl solution and distilled water. The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed by distillation under nitrogen. The crude product was purified by distillation (44 °C/42 mmHg) to give a colorless liquid (20.7 g, 66%). ¹H NMR (CDCl₃, TMS): δ = 2.11 (s, 3H, -CH₃), 2.49 (s, 1H, H-C≡C), 4.68 (s, 2H, HC≡C-CH₂-). ¹³C NMR (CDCl₃, TMS): δ = 20.52, 51.74, 74.70, 77.48, 169.70.

2.2.2 *Synthesis of propargyl trideuterio acetate (2)*

A mixture of 100 mL of benzene, 6.0 g (0.09 mol) of tetradeuteroacetic acid (TCI), 8.4 g (0.15 mol) of propargyl alcohol, and 1.7 g (0.01 mol) of *p*-toluenesulfonic acid (Wako) was refluxed for 6 h with Dean-Stark apparatus. The resulting mixture was washed with a 5% sodium hydrogen carbonate solution and distilled water. After the organic layer was dried over anhydrous sodium sulfate, the solvent was removed by distillation under nitrogen. The crude product was purified by distillation (59 °C/102 mmHg) to give a colorless liquid (3.1 g, 34%). ¹H NMR (CDCl₃, TMS): δ = 2.49 (s, 1H, H-C≡C), 4.68 (s, 2H, HC≡C-CH₂-). ¹³C NMR (CDCl₃, TMS): δ = 20.21, 51.76, 74.71, 77.48, 169.78.

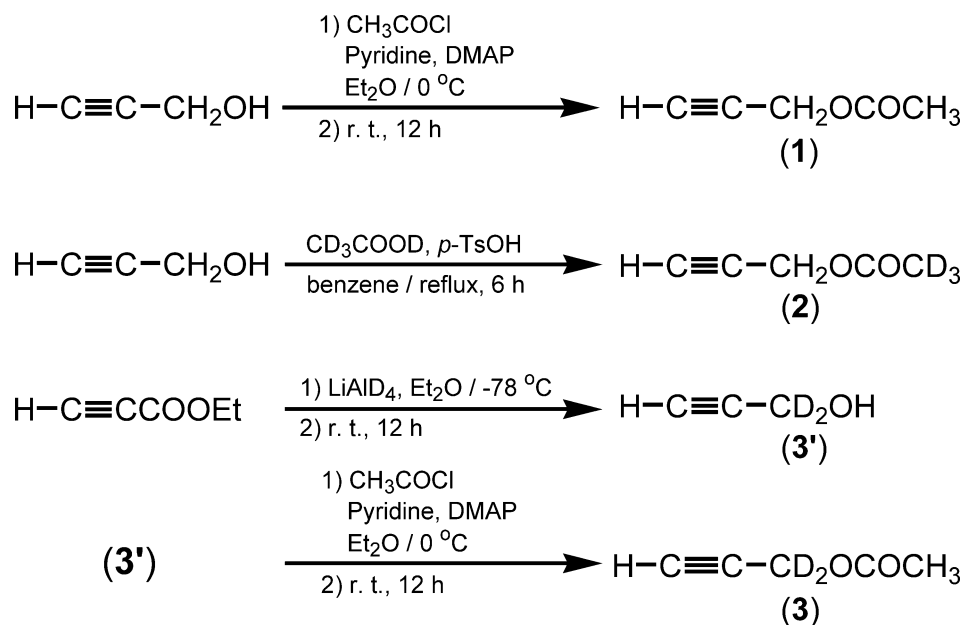
2.2.3 Synthesis of α,α -dideuteriopropargyl alcohol (**3'**)

To a stirred suspension of 5 g (0.12 mol) of lithium aluminum deuteride (LAD) (Taiyo Nippon Sanso) in 540 mL of dry ether, a mixture of 20.6 g (0.21 mol) of ethyl propiolate (TCI) in 160 mL of dry ether was added slowly dropwise. The reaction mixture was stirred for 1.5 h at $-78\text{ }^{\circ}\text{C}$ and then quenched carefully with 10 mL of distilled water, 5 mL of a 15% NaOH solution and 10 mL of distilled water. After stirring for 12 h, the mixture was passed through a short alumina column, and the solvent was distilled off. The crude product was purified by distillation under nitrogen, and the fraction between $60\text{--}108\text{ }^{\circ}\text{C}$ was collected to give the α,α -deuterio-propargyl alcohol (**3'**) as a colorless liquid (4.5 g, 38%), which was used without further purification in the next step.

2.2.4 Synthesis of α,α -dideuterio-propargyl acetate (**3**)

To a stirred mixture of 68 mL of dry ether, 4.5 g (0.08 mol) of the crude α,α -dideuteriopropargyl alcohol (**3'**), 8.8 g (0.09 mol) of pyridine, and 0.95 g (8 mmol) of 4-(*N,N*-dimethylamino)pyridine, a mixture of 7.3 g (0.09 mol) of acetyl chloride in 9.3 mL of ether was added dropwise at $0\text{--}5\text{ }^{\circ}\text{C}$. After stirring for 12 h at room temperature, the resulting mixture was washed with 5% HCl solution and distilled water. The organic layer was dried over anhydrous sodium sulfate, and the solvent was distilled off under nitrogen. The crude product was purified by distillation ($58\text{ }^{\circ}\text{C}/96\text{ mmHg}$) to give a colorless liquid (2.3 g, 28%). ^1H NMR (CDCl_3 , TMS): $\delta = 2.11$ (s, 3H, $-\text{CH}_3$), 2.47 (s, 3H, $\text{H}-\text{C}\equiv\text{C}$). ^{13}C NMR (CDCl_3 , TMS): 20.49, 51.28, 74.66, 77.47,

169.75.



Scheme 2.

2.3 Polymerization

PPAs were obtained by the polymerization of propargyl acetate (PA) initiated with a monodentate Rh catalyst, $[\text{Rh}(\text{nbd})\text{Cl}]_2/\text{NEt}_3$, as shown in Scheme 1. In a typical procedure, 0.1×10^{-3} mol of PA and the calculated amount of the catalyst (0.1×10^{-3} mol) were dissolved in MeOH or NEt_3 solvent using a specially designed U-shaped ampoule [1], and the polymerization was carried out for 4 h at given temperatures in the solvent with constant shaking. The resulting solution was poured into excess amount of MeOH to precipitate a polymer. The resulting polymer was washed with MeOH and dried under dynamic vacuum, *ca.* 10^{-2} torr for 12 h at rt. The yield of the polymer was

determined by gravimetry (Table 1).

Poly(propargyl acetate): poly(1). ^1H NMR (CDCl_3 , TMS): $\delta = 2.05$ (s, 3H, $-\text{CH}_3$), 4.61 (s, 1H, $\text{HC}=\text{C}-\text{CH}_2-$), 6.28 (s, 1H, $\text{HC}=\text{C}-$). ^{13}C NMR (CDCl_3 , TMS): $\delta = 20.6$, 66.6, 128.3, 134.4, 170.5. *Poly(propargyl deuterio-acetate)s: poly(2).* ^1H NMR (CDCl_3 , TMS): $\delta = 4.61$ (s, 1H, $\text{HC}=\text{C}-\text{CH}_2-$), 6.28 (s, 1H, $\text{HC}=\text{C}-$). ^{13}C NMR (CDCl_3 , TMS): $\delta = 20.6$, 66.6, 128.3, 134.4, 170.5. Anal. Calcd for $\text{C}_5\text{H}_3\text{D}_3\text{O}_2$: C, 59.39; H(D), 8.97. Found: C, 57.79; H(D), 8.69. *Poly(α,α -dideuterio-propargyl acetate): poly(3).* ^1H NMR (CDCl_3 , TMS): $\delta = 2.05$ (s, 3H, $-\text{CH}_3$), 6.28 (s, 1H, $\text{HC}=\text{C}-$). ^{13}C NMR (CDCl_3 , TMS): $\delta = 20.6$, 66.6, 128.3, 134.4, 170.5. Anal. Calcd for $\text{C}_5\text{H}_4\text{D}_2\text{O}_2$: C, 59.99; H(D), 8.05. Found: C, 58.72; H(D), 7.80. The elemental analysis for the deuterium was calculated by using the ^1H NMR spectral data of the two deuterated polymers.

3. Results and discussion

3.1 Polymerization

Poly(propargyl acetate)s (PPA)s were obtained by polymerization of monomers **1**, **2**, and **3** using the monodentate Rh catalyst: $[\text{Rh}(\text{nbd})\text{Cl}]_2/\text{NEt}_3$ in MeOH or NEt_3 as the polymerization solvent. The yield with number and weight average molecular weights (M_n and M_w) and its distributions (M_w/M_n), and *cis* % are listed in Table 1. Previously, we have reported that an organic solvent such as MeOH, THF, and NEt_3 with lone pair electrons acts as a good polymerization cocatalyst because the solvent

stabilizes the Rh catalyst as the propagation species which was dissociated to a monodentate Rh catalyst from the bidentate Rh complex catalyst [1,18,19]. However, we found that the highest yield was observed when the polymerization of monomer **1** was performed under the conditions of NEt₃ as the cocatalyst in MeOH at 0 °C (Table 1, run 4). It is noteworthy that aliphatic acetylene ester monomers, e.g., alkylpropiorates unlike this PA monomer did not polymerize in NEt₃ [20]. Poly(**1**) (Table 1, run 5) prepared in MeOH at 40 °C, poly(**2**) and poly(**3**) (Table 1, runs 6 and 7) deuterated at either methyl or methylene moieties, respectively, were used in order to unequivocally determine the spatial geometrical structure of the *cis* and *trans* radicals stabilized in the resulting polymer using the ESR method at room temperature as mentioned below.

Table 1.
Polymerization of PAs using the [Rh(nbd)Cl]₂ catalyst.^a

run	monomer	solvent	cocat. ^b ([M] ₀ /[Cocat.])	temp. (°C)	yield ^c (%)	<i>M</i> _n ^d (/10 ⁴)	<i>M</i> _w / <i>M</i> _n ^d	<i>cis</i> ^e (%)
1	1	MeOH	-	40	trace	-	-	-
2	1	NEt ₃	-	0	43	0.7	1.9	73
3	1	NEt ₃	-	40	43	0.6	1.9	70
4	1	MeOH	100	0	79	0.5	1.8	70
5	1	MeOH	100	40	57	0.5	2.0	77
6	2	MeOH	100	40	44	0.7	1.8	85
7	3	MeOH	100	40	37	0.8	1.9	82

^a [M]₀=0.1 mol/L, [M]₀/[Cat.]=100.

^b NEt₃ was used as cocatalyst.

^c Insoluble fraction in methanol.

^d CHCl₃ soluble part and estimated by GPC(PSt, CHCl₃).

^e CHCl₃ soluble part and determined by ¹H NMR(CDCl₃).

3.2 Polymer structure

The structure of the polymers was elucidated by ^1H NMR and ^{13}C NMR spectroscopies. The ^1H NMR spectra of poly(**1**), poly(**2**), and poly(**3**) are shown in Fig. 1. The ethynyl proton signal, $\text{H}-\text{C}\equiv$, observed at 2.53 ppm in their monomers (**1**, **2**, and **3**) disappeared completely and the new olefinic protons for polyene main-chain, which suggest a *cis-transoid* structure of the main-chain, were observed at 6.28 ppm. The spectra of the deuterated polymers, poly(**2**) and poly(**3**), also supported their structures as shown in Fig. 1. The *cis* % of the polymers in Table 1 were determined according to the method of the literature [1].

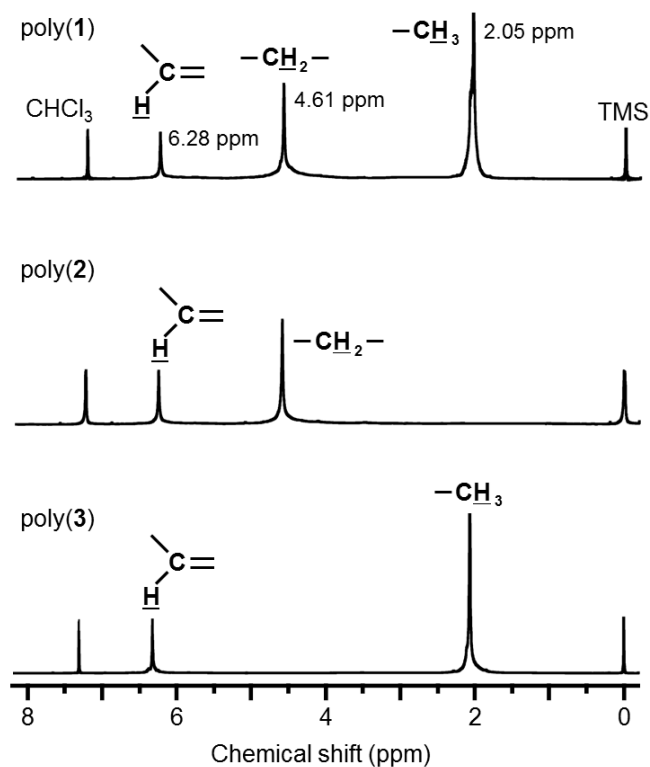


Figure 1.

3.3 ESR spectra

Previously, we reported that the ESR spectra of the radicals of aromatic polyacetylenes were observed before and after compression of the polymers, and the *cis* and *trans* radicals are produced through the *cis*-to-*trans* isomerization *via* the rotational scission of the helical *cis* C=C bond [1a,b,c,d], as shown in Scheme 1. ESR parameters of poly(1), poly(2), and poly(3) are summarized in Table 2. In addition, the *g* value of the observed radicals was used to deduce the geometrical structures, i.e., *cis* form or *trans* form, when one hetero atom such as N, S, and I is involved within the side-chain of the polyacetylene molecules [1e,21-23]. Such a hetero atom has a relatively large spin orbit coupling constant, ζ compared with that of the hydrocarbon atoms [22-24]. We have also revealed that these hetero atom can shift the *g* value to a lower magnetic field, especially in the *cis* form, although such a shift is extremely small for *trans* form, because of spatial decoupling of the magnetic interaction due to the unpaired electron 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 decoupled between the hetero atom in the side-chain and the unpaired electrons in the main-chain.

Table 2.
ESR parameters of PPAs.^a

polymer	radical	<i>g</i> value	a^{H_α}	$a^{H_{\beta_{1,2}}}$	$a^{H_{\beta_{3,4}}}$	a^{H_γ}	ΔH_{msl}^b	spins/g	unit/spin
			(G)	(G)	(G)	(G)	(G)	(/10 ¹⁶)	(/10 ⁵)
poly(1) ^c	<i>cis</i>	2.0044	-	6.0	19.0	-	4.5	1.91	3.21
	<i>trans</i>	2.0027	16.0	-	-	4.0	6.0		
poly(2) ^d	<i>cis</i>	2.0044	-	6.0	19.0	-	4.5	2.75	2.16
	<i>trans</i>	2.0027	16.0	-	-	4.0	6.0		
poly(3) ^e	<i>cis</i>	2.0044	-	6.0	2.9	-	4.5	2.45	2.45
	<i>trans</i>	2.0027	16.0	-	-	4.0	6.0		

^a Observed at room temperature.

^b ΔH_{msl} =line width.

^{c, d, and e} Prepared by using the polymerization conditions of runs 5, 6, and 7 in Table 1.

3.4 Spectral simulation of poly(1)

We examined whether two ESR signals corresponding to the *cis* and *trans* radicals were also observable in case of the freshly prepared poly(1) at room temperature. Consequently, we observed a fairly strong ESR spectrum as shown in Fig. 1a, although the pressure was not imposed to the polymer. To the best of our knowledge such ESR spectrum has never been reported up to date. Therefore, in order to spectroscopically determine whether the two paramagnetic chemical species, i.e., *cis* and *trans* radicals, are generated in poly(1), the so-called microwave power saturation effect was also examined at 1 mW and 0.001 mW, respectively [1d,21]. It was clear that the spectral line shape and its intensity was changed with decreasing microwave power (see Fig. 2b) by which fairly small hyper fine coupling (hfc) pattern compared with that of Fig. 2a were detected. The newly observed coupling pattern may reflect the existence of the two types of radicals involved in the polymer, poly(1). Therefore, in order to obtain

more detailed hfc data for each radical the second derivative ESR spectrum was also measured at a fairly lower microwave power, i.e., 0.001 mW, as shown in Fig. 2c.

As a working hypothesis the ESR spectrum of Fig. 2c is considered to be superimposed with a triple-triplet and a doublet line spectra due to the *cis* and *trans* radicals, respectively, as shown in Fig. 2e with the stick diagram. Such a preliminary assignment may be supported by our previous experimental facts, i.e., the *cis* and *trans* radicals generated in the substituted polyacetylene polymers are observed as the sum of the so-called odd and even line ESR spectra, respectively [1e,5,21].

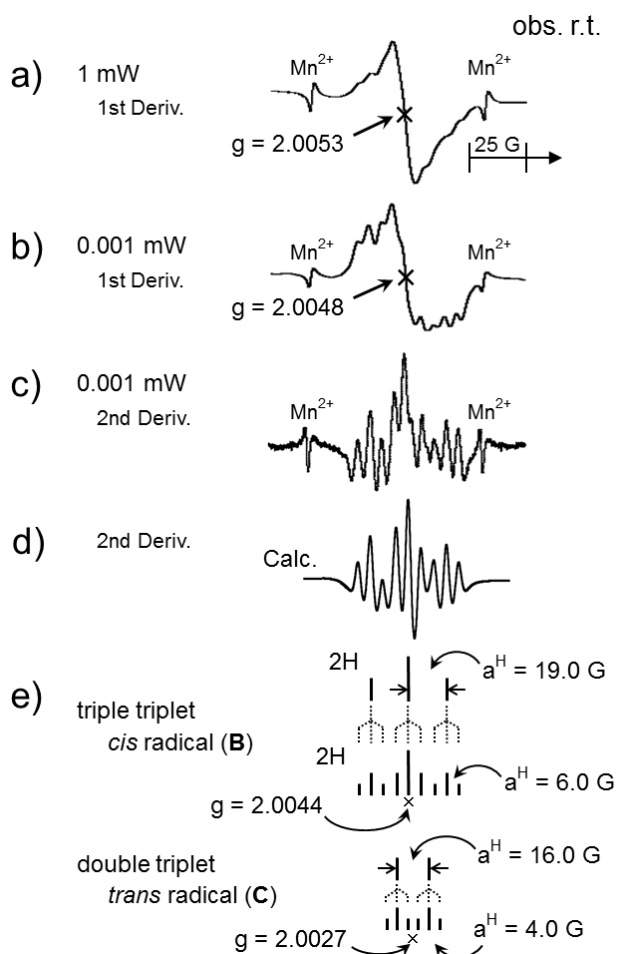


Figure 2.

3.5 Spectral simulation of poly(2)

The poly(2) deuterated at the methyl moiety, $-\text{CD}_3$, in the side-chain gave the completely same ESR spectra as those shown in the Figs. 2a, b, and c. This result strongly indicates that the three protons of the methyl group of the side-chain are never magnetically interacted with the two chemical species, i.e., the *cis* and/or *trans* radicals which are detectable by the ESR technique.

3.6 Spectral simulation of poly(3)

Another deuterated polymer, poly(3), was also examined whether the spectral change is induced at room temperature. The second derivative ESR spectra of poly(3) were also measured at different microwave power of 1 mW and 0.001 mW, respectively, at room temperature. It is clear that notably large spectral changes took place as shown in Figs. 2c and 3b. These spectral change undoubtedly proves that the large triplet line of poly(1) (see Fig. 2e) comes from not the two vinyl protons of the main-chain but the methylene protons in the side-chain of poly(3) (see Schemes 1 and 3). Therefore, according to the stick diagram (see Fig. 2e and 3d) the spectra were successfully simulated assuming that the *cis* radical (**B**) has such the triple-triplet spectrum with the hfc: $a^{\text{H}\beta_3} = a^{\text{H}\beta_4} = 19.0$ G due to the two methylene protons, and $a^{\text{H}\beta_1} = a^{\text{H}\beta_2} = 6.0$ G due to two main-chain vinyl protons, line width, $\Delta H_{\text{msl}} = 4.5$ G and $g = 2.0044 \pm 0.0005$, and the *trans*

radical (**C**) shows a doublet spectrum with a $a^{\text{H}_\alpha}=16.0$ G due to the one main-chain H_α proton, and $a^{\text{H}_{\gamma_1}}=a^{\text{H}_{\gamma_2}}=4.0$ G and line width, $\Delta H_{\text{msl}}=6.0$ G and $g=2.0027$ as shown in Fig. 2e. Thus, the simulated spectrum, Fig. 2d well agreed with that of the observed one, Fig. 2c each other.

The ESR spectrum of poly(**3**) was also simulated by considering the so-called gyromagnetic ratio of the proton and deuteron, $\gamma^{\text{H}}/\gamma^{\text{D}}=6.5$ [22], as shown in Figs. 3b and 3c. Thus, this experiment strongly proves that the observed spectra are undoubtedly superimposed with those of the *cis* and *trans* radicals (**B** and **C**). This also suggests that the highest spin density of the resulting *cis* radical (**B**) localized at not only main-chain protons, H_{β_1} and H_{β_2} , but also the two methylene protons; H_{β_3} and H_{β_4} , in the side-chain of poly(**1**) in Fig 4a, and this result is similar to poly(*p*-halogenated phenylacetylene)s [24] and poly(*p*-sulfoxide phenylacetylene) [21].

On the other hand, the doublet line spectrum as shown in Fig. 1e was reasonably calculated by assuming that only one H_α proton magnetically can couple with the unpaired electron as the *trans* radical as shown in Fig. 4b. In other words, neither the main-chain H_{γ_1} and H_{γ_2} protons nor the side-chain CH_2 protons magnetically couples with an unpaired electron of the *trans* radical because the 2p orbital of unpaired electron and the side-chain plane are spatially perpendicular each other, as shown in Fig. 4b. Thus the *trans* radical was also proven to show ESR spectrum with the simple double triplet line unlike the previous case of the *trans* radicals which were generated by the so-called pressure induced *cis*-to-*trans* isomerization where the *trans* radical hold a fairly planar conjugation structure, i.e., a fairly narrow Lorentzian single line spectrum

was observed and suggested π -conjugation such as the so-called soliton reflecting fast motional narrowing of the unpaired electron [2b,19,26].

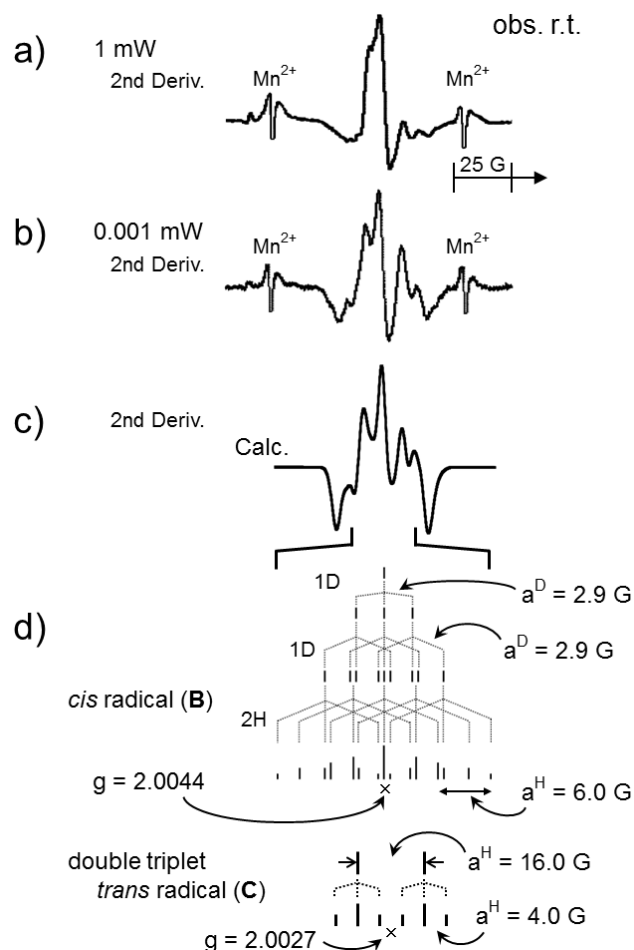


Figure 3.

3.7 Semi-empirical quantum chemical calculation

Conformational analysis using the AM1 program [19] was performed for assuming a model compound of 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 the polymerization but also on standing the polymer solution at room temperature (see Scheme 3). In order to calculate the most energetically stable structure by using the AM1 calculation a model structure which comprises twenty monomer sequences with an unpaired electrons for the *cis* radical was adopted. After that further the simplified *cis* radical model as depicted in Fig. 4a was used to calculate the spin density of the *cis* radical. The AM1 calculation showed that in the *cis* radical the C_α, C_{β1}, C_{β2}, and C_γ takes a planar plane with a sp² configuration and an angle, θ₁ and θ₂=75 °, θ₃ and θ₄=30 °, respectively. The calculation revealed that the spin density appeared at not only ether oxygen, -O-, but also until the carbonyl oxygen, C=O to some extent. This means that the spin density due to unpaired electron generated through the rotational scission of the helical *cis* C=C double bonds in the main-chain can migrate to the methylene moiety and the O-C=O moiety in the side-chain (see Scheme 3). Therefore, according to the AM1 calculation the observed large g value, i.e., 2.0044±0.0005, due to the *cis* radical is reasonably explained by the migration of the spin density to the O-C=O moiety because of its fairly large spin orbit coupling constant, i.e., ζ value as mentioned above and the large ζ value make the g value shift to a lower magnetic field as observed in Figs. 2 and 3. Thus we can successfully explain the reason why the g value of the *cis* radical is fairly large, 2.0044±0.0005 compared to 2.0027±0.0005 of the *trans* radical. The very large spin density can be delocalized even on the ether oxygen and carbonyl oxygen atoms which have also a large orbit coupling constant ζ=151 [22], although the spin orbit coupling constant responsible for the -O-C=O group has been unknown up to date.

The doublet line of ESR as shown in Figs. 2d and 2e may also be reasonably attributed to that of the *trans* radical stabilized in the conjugated main-chain, because the resulting *trans* sequences have a fairly twisted configuration which can localize the spin density as the π -radical, i.e., a planer plane made by the C_α , $C_{\beta'}$, and C_β allow the magnetic coupling between the unpaired electron and H_α to give such a doublet spectra (see Figs. 2d, 2e, 3c, and 3d, and Fig. 4b), though a mobile unpaired electron similar to the so-called soliton of the substituted polyacetylenes has been shown to stabilize in the seven main-chain protons and to give a singlet line spectrum [1d,25,26]. Thus, the AM1 calculation consistently explains our experimental results without problem.

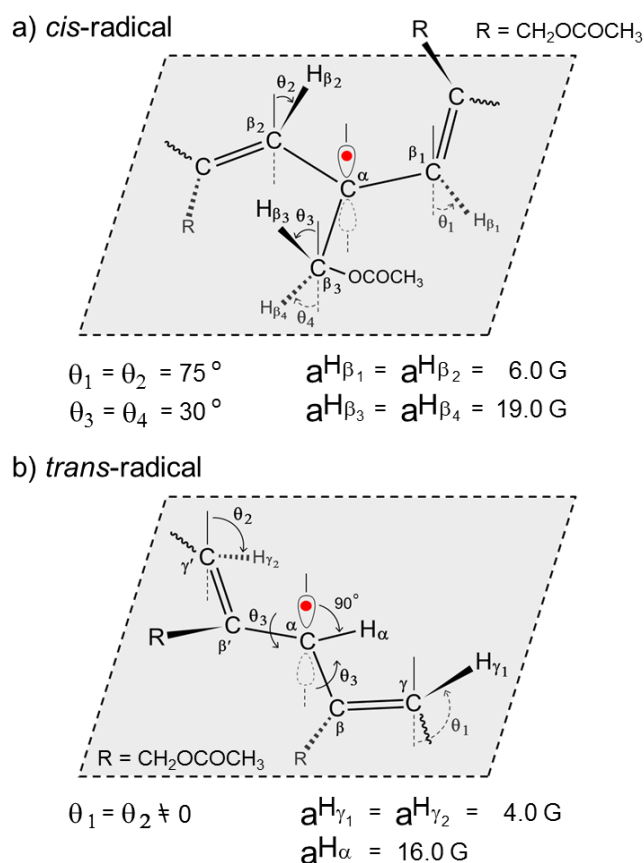
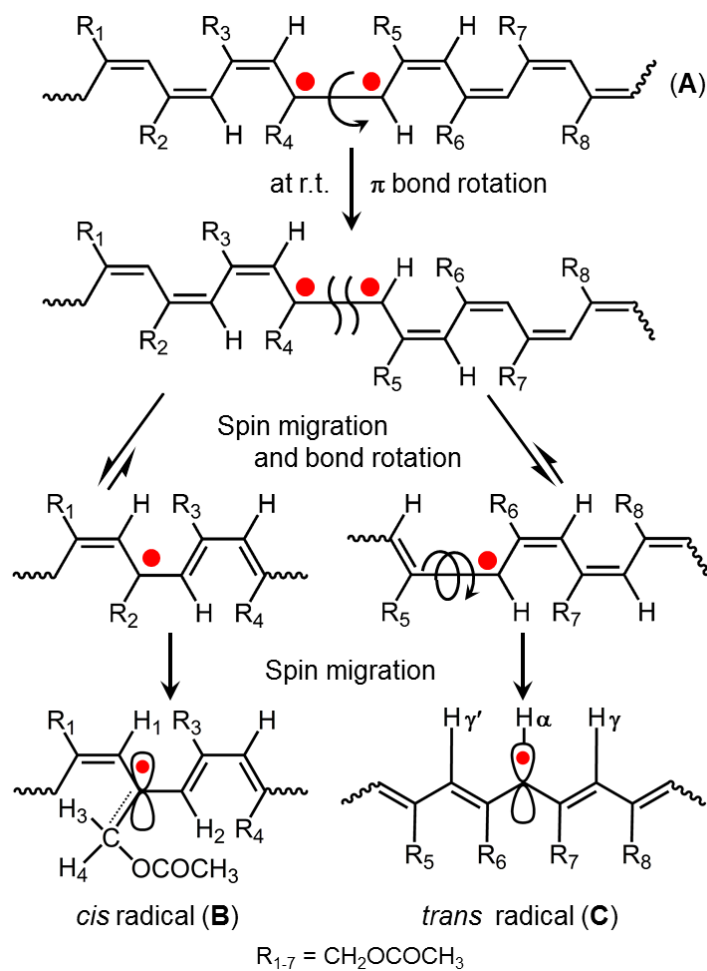


Figure 4.

The aromatic polyacetylenes having a small amount of the spin density at the oxygen atom of the side-chain moiety may show an interesting magnetic behavior like the so-called spin glass as a novel time memory material [13] and become also magnetic materials for a useful radical cell [27].



Scheme 3.

4. Conclusion

The stereospecific polymerization of propargyl acetate and two propargyl acetates analogues deuterated at the either methyl or methylene moiety was successfully

performed using a Rh catalyst, $[\text{Rh}(\text{nbd})\text{Cl}]_2$, MeOH and NEt_3 solvents at 0 and 40 °C and the corresponding *cis-transoid* polymers was obtained selectively in moderate yields. The polymerization even at the temperature induced the *cis-to-trans* isomerization, which was observed by the measurement of the ESR spectra. The ESR spectrum is considered to be composed of the *cis* radical whose spin density migrate to the not only main-chain but also the side-chain, i.e., $-\text{CH}_2-$ and $-\text{O}-\text{C}=\text{O}$ moiety giving the large g value, $g=2.0044 \pm 0.0005$. On the other hand, the spin density of the *trans* radical is localized in the only main-chain which affords a smaller g value compared to that of the *cis* radical, which is a typical hydrocarbon radical.

References

- [1] (a) Tabata M, Takamura K, Yokota Y, Nozaki T, Miyasaka H, Kodaira K. *Macromolecules* 1994;27:6234-36. (b) Tabata M, Tanaka Y, Sadahiro Y, Sone T, Yokota K, Miura I. *Macromolecules* 1997;30:5200-4. (c) Huang K, Tabata M, Mawatari Y, Miyasaka A, Sato E, Sadahiro Y, Kashiwaya Y, Ishii K. *J Macromol Sci Pure Appl Chem* 2005;43:2836-50. (d) D'Amato R, Sone T, Tabata M, Sadahiro Y, Russo MV, Furlani A. *Macromolecules* 1998;31:8660-65. (e) Huang K, Mawatari Y, Tabata M, Sone T, Miyasaka A, Sadahiro Y. *Macromol Chem Phys* 2004;205:762-70.
- [2] (a) Tabata M, Sone T, Sadahiro Y, Yokota K, Nozaki Y. *J Polym Sci Part A Polym Chem* 1998;36:217-23. (b) Mawatari Y, Tabata M, Sone K, Ito Y, Sadahiro. *Macromolecules* 2001;34:3776-82.

- [3] (a) Aoki T, Shinohara K, Oikawa E. *Chem Lett* 1993;22:2009-12. (b) Teraguchi M, Suzuki J, Kaneko T, Aoki T, Masuda T. *Macromolecules* 2003;36:9694-97.
- [4] (a) Suzuki Y, Tabei J, Shiotsuki M, Inai Y, Sanda F, Masuda T. *Macromolecules* 2008;41:1086-93. (b) Tabata M, Sone T, Sadahiro Y. *Macromol Chem Phys* 1999;200:265-82. (c) Nakako H, Nomura R, Tabata M. *Macromolecules* 1999;32:2861-64. (d) Suzuki Y, Tabei J, Shiotsuki M, Inai Y, Sanda F, Masuda T. *Macromolecules* 2008;41:1086-93.
- [5] (a) Yashima E, Maeda Y, Okamoto Y. *J Am Chem Soc* 1998;120:8895-96. (b) Yashima E, Matsushima T, Okamoto Y. *J Am Chem Soc* 1997;119:6345-59. (c) Nonokawa R, Yashima E. *J Am Chem Soc* 2003;125:1278-83.
- [6] Liu JH, Yan JJ, Chen EQ, Lam JWY, Dong YP, Liang DH, Tang BZ. *Polymer* 2008;49:3366-70.
- [7] Dening TJ, Novak BM. *J Am Chem Soc* 1992;114:7926-27.
- [8] (a) Neher D, Wolf A, Bubeck C, Wegner G. *Chem Phys Lett* 1989;163:116-22. (b) Bredas JL, Adant C, Tacks P, Persoons A, Pierce M. *Chem Rev* 1994;94:243-78. (c) Falconieri M, D'Amato R, Russo MV, Furlani A. *Nonlinear Opt* 2001;27:439-42.
- [9] (a) Tabata M, Sone T, Yokota K, Wada T, Sasabe H. *Nonlinear Opt* 1999;22:341-44. (b) Wada T, Wang L, Okawa H, Masuda T, Tabata M, Wan M, Kakimoto MA, Sasabe H. *Mol Cryst Liq Cryst* 1997;294:245-50.
- [10] (a) Korshak YV, Medvedeva TV, Ovchinnikov AA, Spector V. *Nature* 1987;326:370-72. (b) Tyutyulkov N, Müllen K, Baumgarten M, Ivanova A, Tadjer A. *Synth Met* 2003;139:99-7.

- [11] (a) Tabata M, Takamura H, Yokota K, Nozaki Y, Hoshina T, Minakawa H, Kodaira K. *Macromolecules* 1994;27:6234-36. (b) Tabata M, Nozaki Y, Yang W, Yokota K, Tazuke Y. *Proc Jpn Acad* 1995;71:219-24.
- [12] (a) Fisher KH, Herz JA. in “Spin Glass” Cambridge University Press 1991:30. (b) Pregjean JJ, Souletie J. *J Phys* 1980;41:1335-52. (c) Floch L, Hammann F, Ocio J, Vincent M. *Euro Phys Lett* 1992;18:647-52. (d) Xenikos DG, Multer H, Jouan C, Suilpice A, Tholence JL. *Solid State Commun* 1997;102: 681-85.
- [13] (a) Tabata M, Watanabe Y, Muto S. *Macromol Chem Phys* 2004;205:1174-78. (b) Watanabe Y, Muto S, Tabata M. *Jpn J Appl Phys Part 2 Lett* 2004;43:300-2.
- [14] (a) Masuda T, Higashimura T. *Adv Polym Sci* 1986;81:121-65. (b) Masuda T, Tachimori H. *J Macromol Sci Pure Appl Chem* 1994;A31:1675-90. (c) Yang MJ, Sun HM, Ling MF. *Acta Polym Sinica* 2000;2:161. (d) Sun HM, Yang MJ, Ling MF. *Chin Chem Lett* 2000;11:1097-10. (e) Yan MJ, Li Y. *Sens Actuators B* 2002;86:155-59. (f) Zhan XW, Yang MJ, Sun HM. *Macromol Rapid Commun* 2001;22:530-34. (g) Kunzler J, Percec V. *J Polym Sci Polym Chem Ed* 1990;28:1221-36.
- [15] (a) Nomura R, Tabei J, Masuda T. *J Am Chem Soc* 2001;123:8430-31. (b) Gao G Z, Sanda F, Masuda T. *Macromolecules* 2003;36:3932-37. (c) Zhang W, Tabei J, Shiotsuki M, Masuda T. *Polym Bull* 2006;57:463-72 (d) Kishimoto Y, Itou M, Miyatake T, Ikariya T, Noyori R, *Macromolecules* 1995;28:6662-66.
- [16] AM1 calculations were carried out with Spartan’04 Windows ver. 1.03 (Wavefunction, Inc.).
- [17] Lefebvre R, Maruani J. *J Chem Phys* 1965;42:1480-96. The original program for

the computer simulation was modified to superpose two spectra having different g values.

[18] (a) Tabata M, Yang W, Yokota K. Polym J 1990;22:1105-7. (b) Yang W, Tabata M, Yokota K. Polym J 1991;23:1135-38. (c) Tabata M, Yang W, Yokota K. J Polym Sci Part A Polym Chem 1994;32:1113-20. (d) Lindgren M, Lee HS, Yang W, Tabata M, Yokota K. Polymer 1991;32:1532-34.

[19] Sone T, Amato R, Mawatari Y, Tabata M, Furlanl A, Russo MV. J Polym Sci Part A Polym Chem 2006;207:1938-44.

[20] McCulloch AW, McInnes AG. Can J Chem 1974; 52:3569-76.

[21] Huang K, Mawatari Y, Miyasaka A, Sadahiro Y, Tabata M, Kashiwaya Y. Polymer 2007;48:6366-73.

[22] Pshezhetskii SY, Kotov AG, Milincuk VA, Rozinskii VI, Tupikov VI. ESR of free radicals in radiation chemistry. New York Wiley;1972.

[23] Tabata M, Lund A. Chem Phys 1983;75:379-88.

[24] Miyasaka A. Sone T, Mawatari Y, Setayesh S, Mullen K, Tabata M. Macromol Chem Phys 2006;207:1938-44.

[25] (a) Harada T, Tasumi M, Shirakawa H, Ikeda S. Chem Lett 1978:1411-14. (b) Shirakawa H, Ito T, Ikeda S. Macromol Chem 1978;179:1565-73.

[26] Weinberger BR, Ehrenfreund E, Pron A, Heeger AJ, Mac Diarmid AG. J Chem Phys 1980;72:4749-55.

[27] Hustedt E J, Thoman H, Robinson BH, J Chem Phys 1990;92:978-95.

Figure captions

Fig. 1. ^1H NMR spectra of poly(**1**), poly(**2**), and poly(**3**) (300 MHz, CDCl_3) prepared with runs 5, 6, and 7 in Table 1.

Fig. 2. ESR spectra of poly(**1**) (a) observed at 1 mW, (b) observed at 0.001 mW, (c) second derivative ESR spectrum observed at 0.001 mW, (d) simulated spectrum, and (e) stick diagram.

Fig. 3. Second derivative ESR spectra of poly(**3**) (a) observed at 1 mW, (b) observed at 0.001 mW, (c) simulated spectrum, and (d) stick diagram.

Fig. 4. Proposed radical structures for poly(**1**) (a) *cis*-radical and (b) *trans*-radical.

Scheme 1. Polymerization of monomers **1-3** and thermal *cis*-to-*trans* isomerization.

Scheme 2. Synthesis of propargyl acetates (**1**), (**2**), and (**3**).

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