Photoinduced Cis-to-Trans Isomerization of Poly(2-ethynylthiophene) Prepared with a [Rh(norbornadiene)Cl]$_2$ Catalyst. ^{1}H NMR, UV, and ESR Studies

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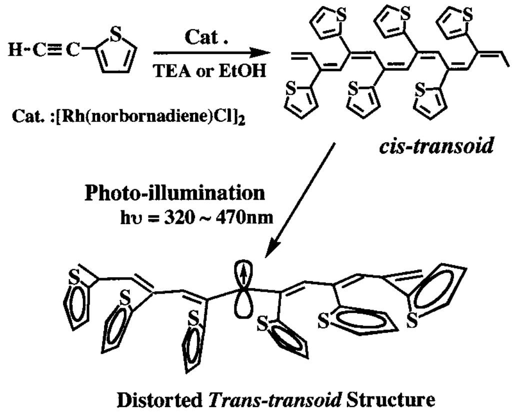
ABSTRACT: Poly(2-ethynylthiophene) was stereoregularly prepared with a Rh complex catalyst, [Rh(norbornadiene)Cl]$_2$, to selectively produce the cis−transoid isomer in high yields when triethylamine was used as the polymerization solvent at 20 °C. Photoinduced cis-to-trans isomerization was newly found to take place when the film of a pristine cis−transoid polymer was photoilluminated using a Xe lamp with light of wavelength, 320−500 nm under vacuum for 5 h. The cis and trans polymers obtained before and after the illumination were characterized in detail using ^{1}H NMR, UV−vis of solution and film, and electron spin resonance methods.

Introduction

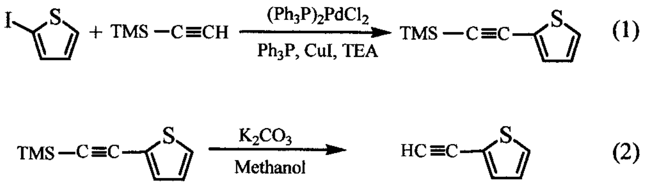
We previously have demonstrated[1−8] that monosubstituted acetylenes such as phenylacetylene derivatives and aliphatic acetylenes, i.e., propiolates called acetylene esters, can be stereoregularly polymerized to selectively afford the corresponding polyacetylene polymers bearing a cis−transoid structure in high yields under mild conditions. We also showed that triethylamine (TEA) or alcohol used as the polymerization solvent works as the cocatalyst.[9−11] Further, the cis−transoid polymer was shown to form a pseudohexagonal structure called a columnar or nanohole assembly as a π-conjugated self-assembly whose diameter can be also easily controlled by the length of the side chain in the polyacetylenes, e.g., from ca.13 to ca. 65 Å.[7,12] In the case of polypropiolate columnar, interestingly, it was evidenced that concentration of oxygen can be enriched from ca. 21% to ca. 40% when the film was once passed through air, irrespective of the fact that the polymer possessed no trimethylsilyl moiety in the molecules.[7,12]

Recently, we found[6] that not only pressure- but also thermal-induced cis-to-trans isomerization takes place for the stereoregular polyacetylenes (see Scheme 1), although the trans isomer obtained by thermal treatment of the cis polymer did not always have such planar trans conjugation sequences but distorted trans sequences where the effective conjugation length is fairly short. In this paper we show the first photoinduced cis-to-trans isomerization regarding the film of the monosubstituted polyacetylene, i.e., poly(2-ethynylthiophene), P2ET, which was prepared with the Rh complex catalyst together with detailed characterization of the polymers obtained before and after the illumination using ^{1}H NMR, UV−vis, and electron spin resonance (ESR) methods. No report on the polymerization of P2ET polymer using [Rh(NBD)Cl]$_2$ catalyst and TEA or alcohol solvent including the photoinduced cis−trans isomerization of P2ET polymer has been published to date, to the best of our knowledge, despite the potential importance of the materials from not only a scientific point of view but also possible industrial applications.[13−18]

Scheme 1. Synthesis and Photoinduced Cis-to-Trans Isomerization of Poly(2-ethynylthiophene)



Scheme 2. Synthesis of 2-Ethynylthiophene



Experimental Section

Materials. 2-Ethynylthiophene (2ET) was prepared according to the literature[19] by the coupling reaction of trimethylsilylacetyelene (Aldrich) with 2-iodothiophene (Aldrich) catalyzed by (Ph$_3$P)$_2$PdCl$_2$ (Aldrich) and followed by deprotection of the trimethylsilyl group (see Scheme 2, eq 2); yields 48%, bp 50 °C/25 mmHg. The resulting monomer was distilled once from CaH$_2$ before use. [Rh(norbornadiene)Cl]$_2$ (Aldrich) was used without further purification. Triethylamine (TEA) was distilled from sodium benzophenone ketyl. Ethanol was distilled once from Mg(OEt)$_2$ and stored under nitrogen over molecular sieve 3A (Merck).

Polymerization. Polymerization was carried out using a U-type glass ampule equipped with two inlets capped with a septum rubber.[8] A typical polymerization procedure is as follows: [Rh(NBD)Cl]$_2$ (13 mg, 0.028 mmol) and a monomer (0.3 g, 2.8 mmol) were placed in each side of the ampule, and

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Table 1. Results of Polymerizations of 2ET Monomer with the Rh Complex Catalyst[a]

run	solvent	[M], mol/L	time, h	yield, %	M_n	M_w/M_n	color
1	TEA	0.5	2	98	19 000	2.8	brown
2	EtOH	0.5	2	34	15 000	2.1	yellow
3	EtOH/TEA	0.5	2	36	17 000	2.3	yellow
4	toluene/TEA	0.5	2	85	37 000[b]	3.6	yellow
5	THF/TEA	0.5	2	75	60 000[b]	4.4	yellow

[a] Polymerization temperature, 20 °C. [b] Bimodal distribution.

a solution of TEA (2.8 mL) or EtOH (2.8 mL) was also introduced to both sides of the ampule. After standing the solutions for 10 min, at 20 °C the monomer solution and the catalyst solution were mixed in order to start the polymerization. After 2 h the resulting P2ET polymer was precipitated into a large amount of methanol, obtained as a brown or yellow powder, filtrated, and dried in vacuo at ca. 10^{-3} Torr for 24 h at room temperature (see Table 1). Elemental analysis of no. 1 in Table 1 as a typical polymer: Calcd (%) for $C_6H_4S_1$ (MW = 108.16): C, 66.6; H, 3.73; S, 29.65. Found: C, 63.67; H, 3.85; S, 27.11.

Characterization. Molecular weights and the molecular weight dispersity of the resulting polymers were estimated by JASCO 900 gel permeation chromatography (GPC) equipped with a refractive index detector using tetrahydrofuran (THF) as the eluent at flow rate of 1.0 mL/min with a Shodex KF-806L column and calibrated with polystyrene standards (see Table 1). ^1H NMR spectra were recorded on a JEOL JNM-A 400 MHz using $CDCl_3$ as solvent at room temperature. UV spectra of solution and film of the polymers were recorded on a JASCO V550 equipped with ISV-469. ESR spectra were observed on a JEOL FE1XG with 100 kHz field modulation at room temperature and 77 K. The cis-to-trans isomerization was performed by photoillumination using a Xe lamp with a band-pass filter in order to pass visible light: 300–470 nm under vacuum.

Photoillumination. The pristine cis polymer was cast from a chloroform solvent on a quartz ampule, $\phi = 3$ mm, $l = 20$ mm which was placed in a wider ESR ampule of $\phi = 7$ mm, $l = 200$ mm for illumination. The wider ampule was evacuated at ca. 10^{-3} mmHg for 2 h at room temperature so as to prevent oxidization of the film during the illuminations and was shielded.

A thin film cast from the pristine cis polymer on a quartz plate of 10 mm × 20 mm × 1.5 mm was used for UV measurement after evacuation at ca. 10^{-3} mmHg for 2 h at room, followed by illumination under nitrogen stream. The two samples were photoilluminated using a USHIO SX-UI 500XQ lamp together with the band filter in order to pass light of 320–470 nm.

Results and Discussion

Polymerization. We previously showed[1−10] that TEA or alcohol is a notably preferred solvent to produce the corresponding aromatic or aliphatic polyacetyelenes bearing a cis–transoid structure as the major component in high yields and worked as the cocatalyst of the Rh complex catalyst, although such solvents have not been used, to the best of our knowledge, to date. The reason may be not only that the solvent is considered unusual in an ordinary polymerization but also that it can deactivate the catalysts such as the Ziegler–Natta catalyst, $Al(Et)_3$–$Ti(On\text{-alkyl})_4$,[20] or metathesis catalyst, e.g., WCl_6 or $MoCl_5$,[21] as the so-called Lewis acids. In this work we also used their solvents in order to determine whether 2-ethynylthiophene, 2ET, monomer containing even a sulfur atom can also be polymerized to produce the cis polymer in high yields. Table 1 shows the results of the polymerization of the thiophene monomer, 2ET, using the Rh complex of the monosubstituted acetylenes under mild conditions.[1−8] It is clear that the polymer yields of ca. 98–75% attained when TEA or its mixed solvents (Table 1, runs 1, 3, 4, and 5) were used for the polymerization solvent even at 20 °C for 2 h where the molecular weight and its polydispersity were estimated as M_n = 15 000–60 000 and M_w/M_n = 2.1–4.4, respectively. It is suggested, however, that in the cases of EtOH, runs 2 and 3 in Table 1, the yield of the polymer was below that attained in the case of the TEA and its mixed solvent, suggesting insufficient dissociation of the Rh complex catalyst as the bidentate complex to the monomeric species responsible for the propagation species of the polymerization as has been deduced by us.[9−11]

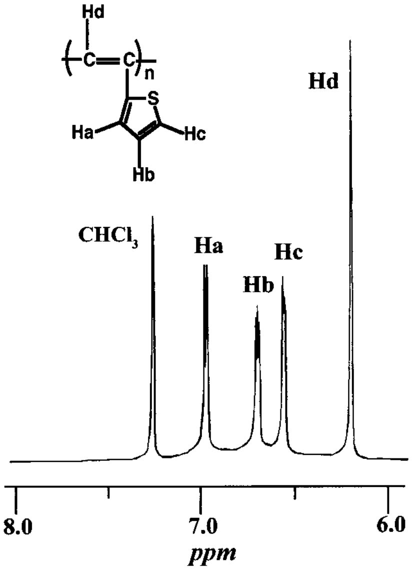

Figure 1. ^1H NMR spectrum of pristine poly(2-ethynylthiophene), P2ET, polymer (Table 1, run 1) observed in $CDCl_3$.

Polystyrenes and aromatic polyacetylenes have been conjectured to have a random coil and rigid-rod-like structure, respectively. Therefore, molecular weights of the polyacetylenes estimated by GPC using the polystyrenes as standard may be larger compared with that of the former polymer.

Figure 1 shows the ^1H NMR spectrum of the resulting P2ET polymer (Table 1, run 1) observed in chloroform solvent at ca. 30 °C. This spectrum featured a typical cis–transoid structure because it is composed of very sharp lines, indicating statistically a very narrow distribution of the chemical shifts due to the highly regular structure.[11] This clearly evidenced that the ratio of an integrated area due to the =C–H proton at 6.2 ppm and three thiophene protons observed at ca. 6.55–6.99 ppm can be estimated rigorously as 1.0:3.0. It seems that neither such a very sharp line width spectra has been observed nor an accurate integration ratio between the peaks of the relevant protons has been obtained when other polymerization catalysts, e.g., metathesis catalyst, $MoCl_5$, or WCl_6, were used.[21] Thus, these results clearly indicate formation of a highly stereoregular cis–transoid polymer. It should be also noted, however, that even when such a heteroatom, i.e., sulfur having a d-orbital, is involved in the monomer molecule, the polymerization is not retarded and/or inhibited by the atom.

Solution UV–vis Spectra. Figure 2 shows the UV spectrum of the brown and yellow polymers (Table 1, runs 1 and 2) which were prepared with TEA and EtOH

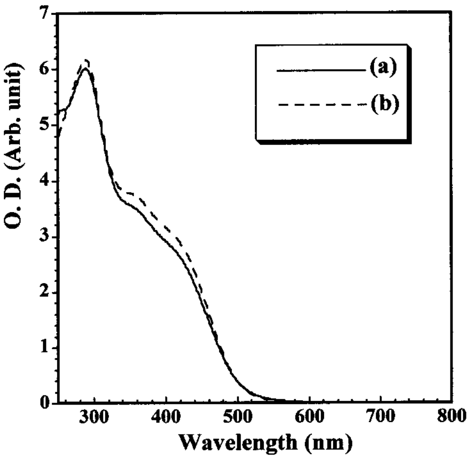

Figure 2. UV spectra of the P2ET polymers (Table 1, runs 1 and 2) observed in $CHCl_3$ solvent. Polymerization solvent: (a) triethylamine (TEA) and (b) ethanol (EtOH).

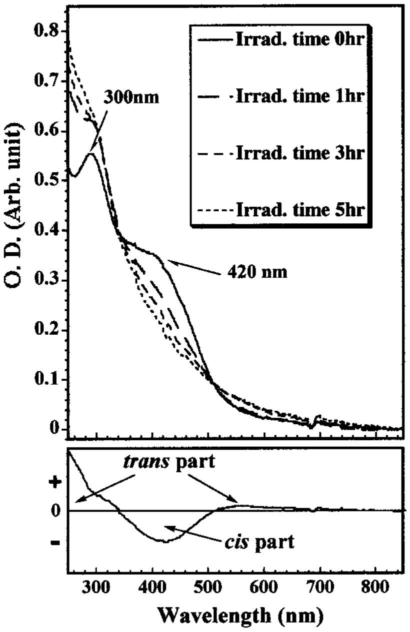

Figure 3. UV spectra of the P2ET polymer observed before and after photoillumination using light of wavelength in the range of 320−470 nm: (a) yellow polymer (Table 1, run 1) and (b) subtraction spectrum.

solvents, respectively, and observed using highly purified spectrograde chloroform. These spectra are almost the same as that of the yellow polymers in Table 1, suggesting that the observed colors of their polymers are not ascribed to that of the primary structure, such as a repeated double-single structure, but rather to the polymer molecular assembly, e.g., a pseudohexagonal structure called columnar as has been proven by us recently.[7,22,23]

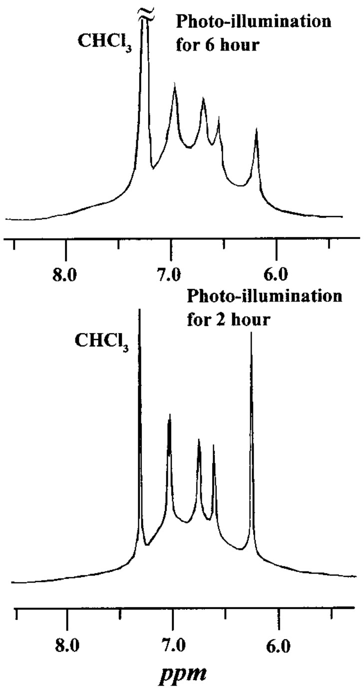

Figure 4. ^1H NMR spectra observed after the photoillumination using light of wavelength in the range of 320−470 nm at room temperature under vacuum: (a) after 2 h and (b) after 6 h.

Photoinduced Isomerization. Figure 3a shows the UV spectra of the film of the pristine P2ET polymer (Table 1, run 1) observed before and after photoillumination using a Xe lamp with a band-pass filter in order to pass wavelength light, 320−470 nm, under vacuum. It is clear that the controlled polymer film shows two peaks at ca. 420 and 300 nm, respectively. Such two peaks are observed even in the solution UV−vis of the pristine polymer. The longer wavelength absorption at ca. 420 nm may be assigned to that of the cis isomer in which a few monomer units containing the side chains and main chains make a chromophore to show such a peak absorption at ca. 420 nm as previously reported by us for aromatic polyacetylenes,[1−6] although the peak at ca. 300 nm may be ascribed to that of the vinylthiophene moiety, suggesting that the plane of the thiophene ring and the cis C═C bond plane are not planar but decline to some extent.[6] We found that the photoillumination of the cis polymer using light of 320−470 nm did dissipate the two absorption peaks completely and, inversely, increased notably the intensity of the lower wavelength absorption region from ca. 350 to ca. 275 nm. The difference spectrum obtained by subtraction of spectra observed before and after the illumination for 5 h is shown in Figure 3b. This difference spectrum clearly indicated that the photoillumination dissipates the broad peak at ca. 420 nm which was assigned to that of the cis isomer and, inversely, increased the absorption peak intensity at the longer wavelength region from 520 to 680 nm which can be ascribed to that of fairly long trans conjugated sequences, although the intensity is not strong. We previously showed[6] that the thermal-induced cis-to-trans isomerization of poly(*p*-nitro(phenyl)acetylene) takes place and generates so-called relaxed *trans*-polyacetylenes which can be considered as distorted *trans*-polyacetylenes where the effective conjugation length is shorter compared with that of the trans sequences which was generated by compression of the cis isomers. It is concluded, therefore, that the trans isomer generated by the illumination has a similar distorted trans conjugated sequence, i.e., shorter conjugation length without any clear absorption peak as observed in Figure 3a.

^1H NMR Spectra after Photoillumination. Figure 4 shows the ^1H NMR spectra observed after the photoillumination of the P2ET polymer (Table 1, run 1) using light of 320−470 nm. The ^1H NMR spectrum of the pristine P2ET polymer is already shown in Figure 1. It is clear that the longer the illumination time, the wider the line width of the spectra is, without large change

Table 2. ESR Parameters of the P2ET Polymers Prepared with the Rh Complex Catalyst[a]

polymer	solvent	temp	g value	ΔH_{msl}, G	spins/ g $\times 10^{18}$	spins/ unit
1	TEA	rt	2.0035	12.8	2.1	1/2700
	TEA	77 K	2.0043	13.0	2.1	
2	EtOH	rt	2.0031	10.5	2.3	1/2700
	EtOH	77 K	2.0035	11.4	2.3	

[a] Polymerized at 20 °C for 2 h.

in the chemical shifts when spectra of Figures 1 and 4 were compared. The spectra observed after the illumination is explained in terms of photoinduced cis-to-trans isomerization, i.e., spectra of Figure 4a,b are superposed with sharp components due to cis structure and broad components due to the resulting trans structure. Such similar spectra have been observed in the case of monosubstituted polyacetylenes which were prepared with the so-called metathesis catalysts or thermal-treated polyacetylenes.[21] The observed line broadening may be interpreted by the so-called dipole−dipole magnetic interaction between the unpaired electrons produced by the rotational scission of the cis double bonds and the protons in the cis and trans isomers, associated with slowing of the molecular motion of their isomers in the chloroform solution.

ESR Spectra. ESR spectra were observed in order to determine the geometrical structures of the pristine brown polymer (Table 1, run 1). Table 2 shows the ESR spectral parameters of the brown polymer in the case of the TEA solvent. The ESR parameters of the brown polymer were determined as $g = 2.0035$ and line width, $\Delta H_{msl} = 12.8$ G at room temperature and $g = 2.0043$ and $\Delta H_{msl} = 13.0$ G at 77 K. On the other hand, in the case of the EtOH solvent (Table 1, run 2), the parameters of the pristine yellow polymer were also estimated as $g = 2.0031$ and $\Delta H_{msl} = 10.5$ G at room temperature and $g = 2.0035$ and $\Delta H_{msl} = 11.4$ G at 77 K. These data strongly support that the resulting P2ET polymer was stereoregularly prepared to selectively produce the cis−transoid polymers, because the observed g values agreed with those of the typical cis isomers containing such a heteroatom, i.e., O or N in the poly(n-alkoxyphenyl)acetylene[1−6] or poly(p-nitrophenyl)acetylene[6] whose spin−orbit coupling constant: δ is fairly large compared with that of a carbon atom.[1−6,24,25] The observed g value and temperature dependency of the line width observed at room temperature and 77 K did not allow us to assign the pristine P2ET polymer to the corresponding trans isomer but to the cis polymer, because usually the g value in the trans isomer is similar to that of a free electron, i.e., 2.0023−4, which is fairly different from the g values shown in Table 2. The π conjugation between the cis double bonds in the main chain and the thiophene moiety plane operates fairly; i.e., the main chain plane is nearly in-plane to that of the thiophene ring plane to give such a larger g value compared with that of the planar trans isomer as previously reported by us.[6,24,25] In the planar trans isomer the trans conjugation sequence plane is nearly perpendicular to that of the thiophene ring in the polymer where no stronger magnetic interaction between the unpaired electrons in the main chain and the sulfur atom in the thiophene should be expected to give a rather large g value as mentioned below (see Scheme 1). This is also supported by small temperature dependencies of the line widths observed in the pristine polymers (see Table 2), indicating that no significant motional narrowing effect due to the mobile unpaired electrons is induced in such a cis isomer,[26,27] because of narrow and restricted conjugation ranges compared with that of the trans isomer bearing longer planar conjugation sequences. Thus, the ESR parameters strongly evidenced that the resulting polymer has a typical cis−transoid structure shown in Scheme 1.

Table 3. Time Dependencies of ESR Parameters of the P2ET Polymer Observed during the Photoillumination

time, h	g value	ΔH_{msl}, G	spin concn $\times 10^{18}$ spin/g
0	2.0036	14.3	2.1
1	2.0035	14.8	260
2	2.0034	14.5	321
3	2.0034	13.1	326
4	2.0034	14.0	323

The ESR parameters observed before and after the illumination using the band filter in order to pass the light of 320−470 nm at 20 °C are shown in Table 3.

The line widths of the powder and its film for the brown cis polymer (Table 1, run 1) were estimated as 12.8 and 14.3 G, respectively (see Tables 2 and 3). This difference may be ascribed to the conformation and/or morphology of the powder and film polymers.

The photoillumination did not induce appreciably increase of the line width in the ESR spectra but rather slightly decreased the line width as shown in Table 3. This strongly indicates that the illumination never induces the so-called cross-linking between the intra- and/or intermolecular chains during the photoinduced cis-to-trans isomerization. This result was also supported by an important experimental fact that the photoillumination never increased the molecular weight but rather decreased, i.e., from $M_n = 19{,}000$ to $M_n = 9800$ for only 2 h at room temperature. This photoinduced cis-to-trans isomerization through the rotational scission of the cis double bonds was also supported by the fact that during the illumination the spin concentration is not decreased but increased with irradiation time from ca. 2.1×10^{18} to ca. 1.37×10^{20} spins/g.[26] Thus, the observed increase of the spin concentration strongly proves formation of trans conjugation lengths as mentioned above.

The slight decrease observed in the line width may be explained by the increase of motional narrowing rate of the resulting mobile unpaired electrons, which are created by rotational scission of the original cis C═C double bonds. This means that the resulting trans sequences are not completely planar but bent and/or distorted structures where effective trans sequence length is shorter compared with that of the extended planar trans sequences.[6] This distortion is supported by the UV−vis spectrum of the polymer film which was photoilluminated for 5 h as shown in Figure 3. The UV−vis spectrum has no sharp absorption peak in the range from 275 to 850 nm, irrespective of trans polyacetylene polymers.[28] Further, the observed increment of the spin concentration proves that the photoilluminated cis-to-trans isomerization resulted in not direct but rotational breakage of the cis C═C bonds in the main chain of the polymer.

It is noteworthy, however, that the observed spin concentration, $\sim 2.0 \times 10^{18}$ spins/g, in the P2ET polymer is fairly high, around 2 orders of magnitude compared with that, ca. 10^{16} spins/g, of ordinary nonsubstituted *cis*-polyacetylenes.[27] This value is rather comparable to that of trans polyacetylene which was prepared using the Ziegler−Natta catalyst at room temperature where one unpaired electron is stabilized in ca. 3000 carbons in the *trans*-polyacetylene, although, inversely, one electron is stabilized in ca. 30 000 carbons in the *cis*-polyacetylene.[26] This indicates that the spin concentrations of the P2ET polymer observed before and after the illumination are clearly comparable not to that of cis but that of trans in the nonsubstituted polyacetylene.

Thus, the ESR data clearly evidenced that the initial and irradiated P2ET polymer can be ascribed to the cis−transoid and trans−transoid polymers, respectively, although the reason why the cis P2ET polymer can stabilize such large amount of radical spins remains to be examined.

Conclusion

2-Ethynylthiophene was successfully polymerized using a $[Rh(norbornadiene)Cl]_2$ catalyst in the presence of triethylamine or ethanol as the polymerization solvent to produce the poly(2-ethynylthiophene), P2ET, polymers. The resulting polyacetylenes were characterized in detail using ^1H NMR, solution and film UV−vis, and ESR methods. The difference in the color of their polymers prepared using TEA or EtOH solvent was suggested in terms of the difference in the degree of the aggregation of the polymer chains. Photoinduced cis-to-trans isomerization of the pristine polymer was newly found to occur when the polymer was irradiated using light of 320−470 nm under vacuum for 5 h.

The obtained trans isomer was also studied in detail using ESR and UV−vis spectra. The data showed that the distorted trans conjugation sequences were formed in the solid phase where a large number of radicals produced by the rotational scission of the cis C═C bonds is stabilized.

Studies on the reason why the P2ET polymer can stabilize such large amount of π radicals is in progress in our laboratory at present together with another ethynylthiophene polymer, and the results will be published elsewhere soon.

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