

Novel Conjugated Polymer Containing Anthracene Backbone: The Microstructure of Polymer Composed of 1,4-Benzenedithiol with 9,10-Diethynylanthracene and Isomerization of the Polymer and Model Compounds

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ABSTRACT: In order to determine the microstructure of the polymer composed of 1,4-benzenedithiol with 9,10-diethynylanthracene (3), the *cis* and *trans* model compounds (1), (2) were prepared. In comparison with the characteristic absorption peaks of vinylene in the model compounds, the microstructure of the polymer was evaluated. Regardless of the initiation mode, UV irradiation, AIBN and none, the *cis* contents of the polymers were almost in the range of 80 to 85%. The behavior of the isomerization of the polymer was also investigated by UV irradiation. The *cis* configuration of the polymer isomerized gradually to the *trans* one with increase of the UV irradiation time. The characteristic features of the isomerization were also studied using model compounds. The *cis* isomer of the model compound undergoes irreversible isomerization to the *trans* one by UV irradiation. In the presence of a radical source in the reaction system, both the *cis* and *trans* isomers can isomerize and reach an equilibrium state after reaction for a sufficient time. The isomerization mechanism was also discussed based on the potential energy diagram.

KEY WORDS Conjugated Polymer / Polymer Microstructure / 1,4-Benzenedithiol / 9,10-Diethynylanthracene / IR Spectra / Model Compound / Photoisomerization / Thermal Isomerization / Potential Energy Surface / Excitation State /

Recently, many kinds of conjugated polymers containing aromatic rings and a sulfur in the polymer backbone have been synthesized by the addition polymerization of dithiol derivatives to diethynyl derivatives.¹⁻³ These polymers have attracted a great deal attention at present because of their unusual electronic and optical properties.^{1,2} For example, the crystallinity of the polymer obtained in the addition polymerization of 1,4-benzenedithiol to 1,4-diethynylbenzene in solid state by UV irradiation could be reversibly changed by the irradiation of characteristic lights. The isomerization of the *cis* to *trans* configuration seems

to induce decrease in the crystallinity of the polymer by a destruction of the semi-stable layer structure of the polymer.⁴

In this series, the authors reported the addition polymerizations of 1,4-benzenedithiol and 9,10-anthracenedithiol to 9,10-diethynylanthracene.^{5,6} These polymers containing anthracene rings in the polymer backbone exhibited high orientation and crystallinity caused by the accumulations or the aggregation of anthracene rings in the polymers. The anthracene unit in the polymer backbone provides an excellent conjugated π system along the polymer chain that is necessary for the high

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nonlinear optical activity (molecular susceptibility).^{7,8} The relations between these physical properties and the microstructure of these anthracene containing polymers are under investigation at present.

This paper deals with the determination of the microstructure of the polymer composed of 1,4-benzenedithiol with 9,10-diethynylantracene and the elucidation of the isomerization behavior of the polymer and model compounds.

EXPERIMENTAL

Monomers

1,4-Benzenedithiol (BDT)² and 9,10-diethynylantracene (DEA)⁵ were synthesized according to the references. Thiophenol (Wako Pure Chemical Industries) was purified by distillation under reduced pressure before use.

Addition Polymerization

The addition polymerization of BDT to DEA was carried out in a pyrex tube in THF at 50°C by UV irradiation, using high pressure mercury lamp 450W (Ushio Co.) under nitrogen atmosphere. The precipitated polymer as an insoluble polymer was recovered by a centrifugation, washed with THF several times and dried *in vacuo* at room temperature overnight. The soluble polymer in the residue was poured into a large excess of methanol and the precipitated polymer was recovered as a soluble polymer by a centrifugation, washed with methanol several times and dried *in vacuo* at room temperature overnight. These obtained

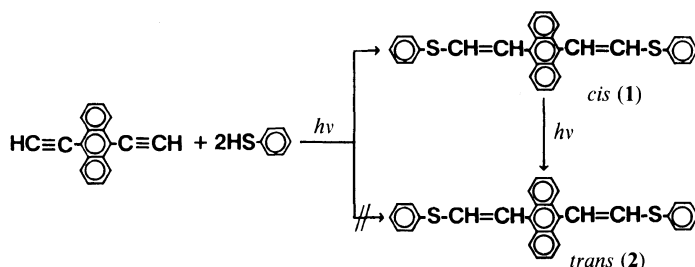
polymers were weighed to calculate the yields and characterized.

Preparation of the Model Compounds

The *cis* and *trans* isomers of the model compounds, 9,10-bis(phenylthiovinylene)anthracene were prepared following the scheme shown below (Scheme 1).

9,10-Diethynylantracene (0.34 g, 0.0015 mol) and thiophenol (0.33 g, 0.0030 mol) in THF (50 ml) were charged in a pyrex tube under nitrogen atmosphere, then, it was irradiated by UV light for 15 min. The reaction proceeded almost quantitatively, and gave a mixed product containing all-*cis* isomer, *cis-trans* isomer and benzenedisulfide. After the purification by an activated alumina column using equivolume mixture of hexane and benzene as an eluent, and then recrystallization in chloroform, a pure *cis* isomer (**1**) was obtained with about 34% yield. mp: 241–242 °C. Sulfur content: calcd. 14.4%, found. 14.3%. MS: M^+ , 446; $M+1^+$, 447. ¹H NMR (in CDCl₃ at 25°C), δ (ppm): 8.26 (q, anthracene ring, 2H), 7.54 (q, anthracene ring, 2H), 7.38–7.20 (m, benzene ring, 5H), 7.24 (q, *cis* vinylene, 2H); J_{cis} , 10.01 Hz. UV (in THF at 20°C): λ_{max} , 401.8 nm (ϵ , 13,500 l mol⁻¹ cm⁻¹).

The *trans* isomer (**2**) could not be synthesized directly by the irradiation of UV light to the mixture of DEA and thiophenol. It was prepared by the isomerization of the *cis* isomer obtained by the above procedure. The *trans* isomer was also purified by the activated alumina column and the recrystallization in acetone before characterization. Yield: 32%. mp:



Scheme 1.

192–193°C. Sulfur content: calcd. 14.4%, found. 14.4%. MS: M^+ , 446, $M+1^+$, 447. ^1H NMR (in CDCl_3 at 25°C), δ (ppm); 8.32 (q, anthracene ring, 2H), 7.54–7.49 (m, anthracene and benzene rings, 5H), 7.38–7.26 (m, benzene ring, 2H), 7.09 (q, *trans* vinylene, 2H); J_{trans} , 15.38 Hz. UV (in THF at 20°C): λ_{max} , 404.6 nm (ϵ , 13,400 $\text{l mol}^{-1} \text{cm}^{-1}$).

Characterization

The following instruments were used for the characterization of model compounds and polymers: ^1H NMR: JEOL PMX-60si, JEOL JNM FX-400; IR: Hitachi 260-50, FT-IR JEOL JIR-5300; UV: Shimadzu UV-260; Mass spectra: JMS D-300. The contents of sulfur in model compounds were determined by means of Schoeniger's method.¹ The molecular weight of the polymers was measured by the method of end group determination, so called copper acetylide method.¹

RESULTS AND DISCUSSION

Previously, the authors synthesized a novel conjugated polymer containing anthracene and sulfur in the polymer backbone (3) by the addition polymerization of BDT to DEA (Scheme 2).⁵

The obtained polymer does not dissolve in any conventional organic solvents, so that infrared spectroscopic measurement by KBr disk method was mainly used to investigate the polymer structure. However, the configuration of the vinylene unit in the polymer backbone has been as yet unknown.

Preparation of Model Compounds

To determine the microstructure of the polymer (3), the authors used a comparative method of the IR spectra between the polymer

and those of model geometrical isomers. These model compounds were prepared according to the Scheme 1: the *cis* isomer was synthesized by radical addition of thiophenol to DEA in THF; the *trans* one was obtained by the UV-induced isomerization of the *cis* one (Details see EXPERIMENTAL).

Figure 1 shows the IR spectra of the model compounds (*cis* and *trans* isomers) measured by KBr disk method. The characteristic absorption peaks of the vinylene out-of-plane deformation vibration were observed at 1320 cm^{-1} (*cis* isomer) and 945 cm^{-1} (*trans* isomer), respectively. This assignment of these characteristic vinylene peaks was undertaken in comparison with the *cis* and *trans* adducts prepared from the radical addition of thiophenol to phenylacetylene.⁹ The extinction coefficient (ϵ) of the *cis* isomer at 1313 cm^{-1} is $98.4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and that of the *trans* one at 945 cm^{-1} is $130.7 \text{ l mol}^{-1} \text{ cm}^{-1}$ in CS_2 at 25°C measured by FT-IR (JEOL JIR-5300). The ϵ of the *cis* and *trans* vinylene in the polymer cannot be determined in common organic solvents because of their insolubility. Accordingly, the *cis* and *trans* contents of the

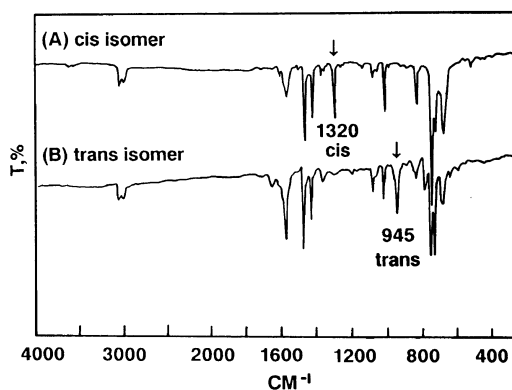
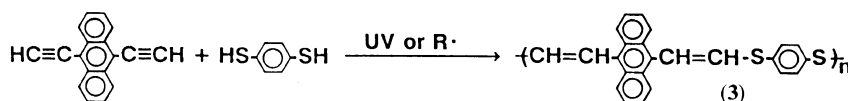


Figure 1. IR spectra of (A) *cis* isomer, (B) *trans* isomer of model compound, 9,10-bis(phenylthiovinylene)anthracene in KBr disk method.



Scheme 2.

vinylene in the polymer backbone were indirectly estimated with KBr disk method by using the ϵ values of the *cis* and *trans* isomers of model compounds in CS₂. The characteristic band of the *cis* vinylenes at 1313 cm⁻¹ measured in CS₂ shifted to 1320 cm⁻¹ by KBr disk method. The coefficients in the Morero¹⁰ type equations were calibrated with 7 samples comprising *cis* and *trans* isomers at various ratios as well as the errors are controlled in the order of 2%. Then, the concentrations of the *cis* vinylenes (*cis* %) and the *trans* one (*trans* %) of the polymer backbone were determined by the following equations, where D_{1320} and D_{945} mean absorbances at 1320 and 945 cm⁻¹, respectively.

$$C = 3.98 \times 10^{-3} D_{1320} - 4.02 \times 10^{-4} D_{945}$$

$$T = 4.20 \times 10^{-3} D_{945} - 2.43 \times 10^{-4} D_{1320}$$

$$cis(\%) = C/(C+T) \times 100$$

$$trans(\%) = T/(C+T) \times 100$$

Microstructure of Polymers

Figure 2 shows the IR spectrum of the polymer obtained by UV irradiation. The IR spectra of the other polymers synthesized in the presence of AIBN or without any initiator are the same as that obtained by UV irradiation. The characteristic absorption peaks of

the *cis* and *trans* vinylenes in the polymer backbone were observed at 1320 cm⁻¹ and 945 cm⁻¹. Using the above equations the microstructure of the polymer is estimated to be that the *cis* vinylenes content is 85% and the *trans* one is 15%.

Table I summarizes the effect of the initiation mode on the microstructure of the polymers. The polymerization of BDT to DEA was carried out in tetrahydrofuran (THF) at 50°C under nitrogen atmosphere. Previous studies⁵ on the polymer structure showed that the resulted polymer has an alternating structure composed of BDT with DEA. The yield of the polymer obtained without initiator (Table I, No. 5) is relatively high, which would

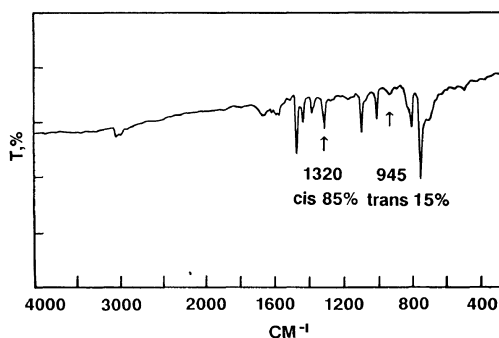


Figure 2. IR spectrum of the insoluble polymer composed of BDT with DEA in KBr disk method (Table I, No. 1).

Table I. Effect of initiation mode and polymerization time on the polymerization of benzenedithiol to diethynylanthracene in THF at 50°C under nitrogen atmosphere^a

No.	Initiation mode ^b	Polymerization time min	Yield/%		$\bar{M}_n \times 10^{-3}$ ^c		<i>cis</i> % ^d	
			Insol.	Sol.	Insol.	Sol.	Insol.	Sol.
1	UV	10	16	61	67	4.0	85	83
2	UV	25	35	45	70	4.2	83	80
3	UV	120	55	21	89	6.7	75	73
4	AIBN	20	48	26	67	4.2	81	85
5	None	20	27	44	58	3.4	85	87

^a [BDT]₀ = [DEA]₀ = 0.085 mol l⁻¹.

^b None: in dark; [AIBN]₀ = 0.0016 mol l⁻¹; UV: High pressure mercury lamp, 450 W.

^c Copper acetylide method.

^d IR method.

be due to the presence of a small amount of oxygen remaining in the reaction solution. The THF solvent was treated previously with NaOH and then refluxed over sodium wire for one or two days and distilled under nitrogen atmosphere before use. Therefore, the existence of a peroxide may be neglected. Regardless of the initiation mode, the obtained insoluble and soluble polymers are abundant in the *cis* vinylene content, reaching above 80% except for No. 3 in Table I.

Figure 3 shows the effect of polymerization time on the microstructure and the number-average molecular weight (\bar{M}_n) of the polymers. The molecular weight of the insoluble and the soluble polymers increased gradually with the polymerization time. This behavior indicates that polymerization progresses stepwise in a similar manner to a condensation polymerization. On the other hand, both the insoluble and soluble polymers maintain high *cis* contents in the beginning of the polymerization, and then gradually decrease with polymerization time. This means that the *cis* vinylene in the polymer backbone isomerizes easily to the *trans* one by UV irradiation with the proceeding of the polymerization,

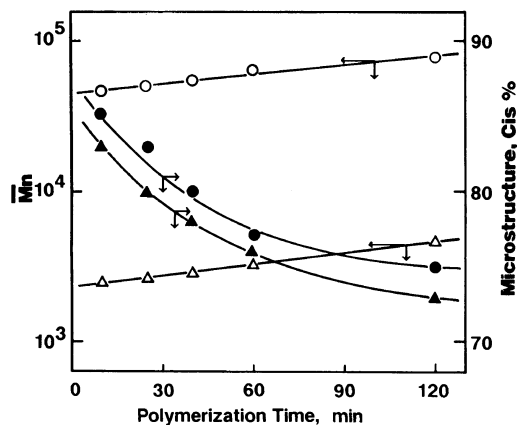


Figure 3. Relation between polymerization time and \bar{M}_n and the microstructure of the polymers polymerized in THF at 50°C by UV irradiation under nitrogen atmosphere: $[\text{BDT}]_0 = [\text{DEA}]_0 = 0.085 \text{ mol l}^{-1}$; ○ and ● indicate the insoluble polymer; △ and ▲ show the soluble polymer.

or the configuration of the polymer growing end would be favorable to connect with reactive end groups of monomers and oligomers in the *trans* form. These problems will be discussed later on.

Isomerization of Polymers by UV Irradiation

As shown in Figure 3, the *cis* content of the polymer decreases with increasing polymerization time. It seems that the vinylene unit in the polymer chain undergoes isomerization from the *cis* configuration to the *trans* one, that is, the polymer chain may adopt a more energetically favorable configuration in which the vinylene unit in the polymer chain would take the *trans* configuration. To confirm this, the resulting insoluble polymer (a point at 120 min. in Figure 3) was isolated and used to make a KBr disk, which is directly illuminated by UV light. As shown in Figure 4, even in the solid state, the vinylene unit in the polymer backbone isomerized from the *cis* configuration to the *trans* one. About 30% of the *cis*

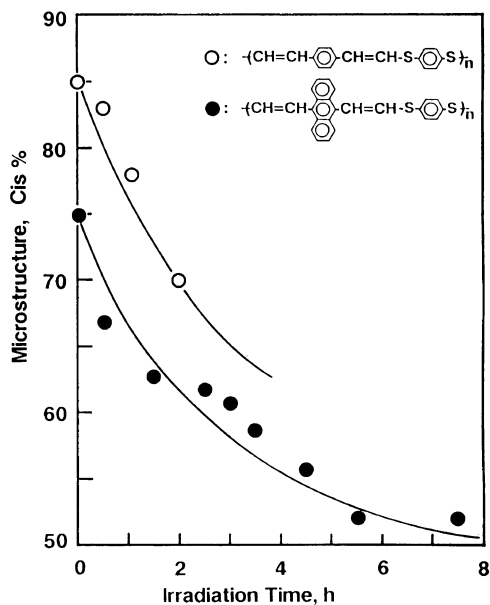


Figure 4. Isomerization behavior of insoluble polymers at 30°C: ●, by UV irradiation under air; ○, by visible light at 539.6 nm under nitrogen atmosphere (KBr, disk).⁴

vinylene compared to the starting state isomerized to the *trans* one after 5 h. This explains that the polymer composed of BDT with DEA easily isomerizes from the *cis* to the *trans*, when a sufficient excitation energy is afforded by UV irradiation. The *cis*-to-*trans* isomerization occurred quickly at the beginning, and then turned smooth. The *cis* vinylene content decreased to 52% after about 8 h. The restriction of the polymer conformation, the interaction to the matrix and the decrease in a transparency of KBr disk may interfere with fast isomerization.

Like the polymer composed of BDT with DEA, the polymer of BDT and 1,4-diethynylbenzene can also isomerize from the *cis* configuration to the *trans* one.⁴ Within 2 h, the *cis* content decreased from 85% to 70% by the irradiation of visible light (539.6 nm).⁴ In this polymer, another interesting feature is that the crystallinity of the polymer obtained in solid state polymerization also decreases with decreasing the *cis* vinylene content in the polymer backbone. It seems that the isomerization of microstructure of the polymer would induce the reconstruction of the polymer crystalline phase.

Isomerization of Model Compound by UV Irradiation

The isomerization of model compound, 9,10-bis(phenylthiovinylene)anthracene by UV irradiation or in the presence of a radical source was also studied. The *cis* isomer of the model compound in a pyrex tube equipped with a three-way stopcock was irradiated in THF by UV light at 25°C under nitrogen atmosphere. After a certain period, a definite fraction was taken out from the reaction tube, and then, the solvent was removed by evaporation under reduced pressure. Successively, it is dried *in vacuo* at room temperature and used to determine the *cis* content by the IR method.

As shown in Figure 5B, the *cis* isomer was converted quickly into the *trans* one by UV irradiation, and the isomerization proceeded completely after 3 h. On the other hand, the resulting *trans* isomer did not come back to the *cis* one under the same conditions. This behavior is different from the UV-induced isomerization of β -phenylthiostyrene (Figure 5A), in which the isomerization of the *cis* and *trans* isomer was carried out in hexane at 30°C under nitrogen atmosphere by UV irradiation, respectively. Both the *cis* and the *trans* isomers

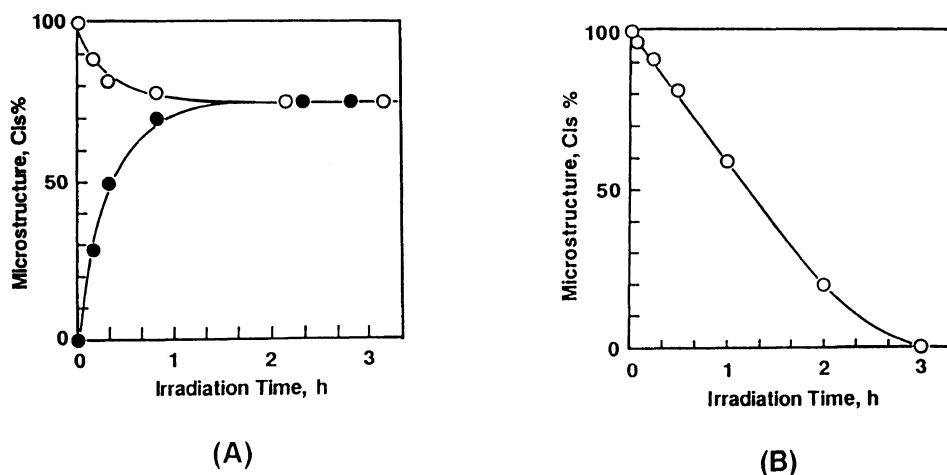


Figure 5. Isomerization of model compounds by UV irradiation: (A) β -phenylthiostyrene in hexane at 30°C under nitrogen atmosphere, $[cis]_0 = [trans]_0 = 0.67 \text{ mol l}^{-1}$ (NMR method).¹¹ (B) 9,10-bis(phenylthiovinylene)anthracene in THF at 25°C under nitrogen atmosphere, $[cis]_0 = 0.026 \text{ mol l}^{-1}$ (IR method).

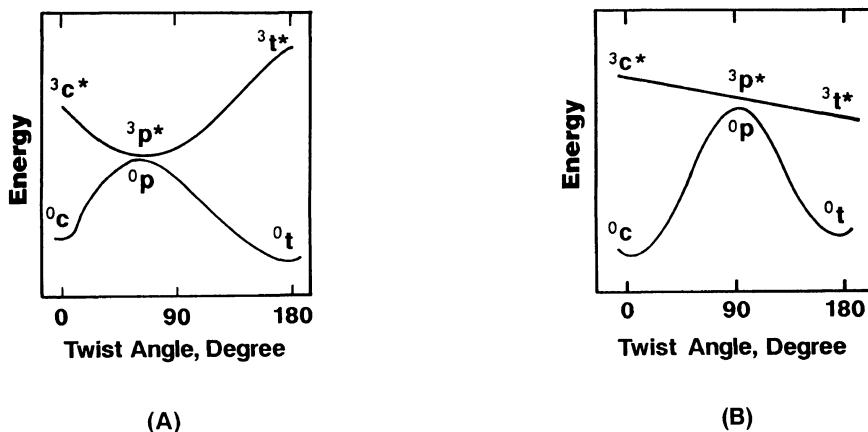


Figure 6. Potential energy surface for isomerization of vinylene bond by UV irradiation: (A) β -phenylthiostyrene,¹¹ calculated by MINDO/3. (B) 9,10-bis(phenylthiovinylene)anthracene expected based on the experimental results.

could undergo isomerization to the opposite configuration, and reached a photostationary state of the *cis* 75% and the *trans* 25% after 2 h.¹¹ Similarly, such characteristic isomerization behavior was also observed in the photoisomerization of stilbene and β -anthryl-ethylene type compounds.¹² The former attained a photostationary state and the latter gave only the *trans* isomer.

This behavior can be accounted for on the basis of the energy levels of the transition states for the isomerization. Figure 6 shows the relationship between the potential energy surfaces of the compounds and the twist angle around their vinylene bond.

In the case of β -phenylthiostyrene (Fig. 6A), UV-induced excitations of *cis* and *trans* isomers give *cis* triplets ($^3c^*$) and *trans* triplets ($^3t^*$), respectively. However, neither $^3c^*$ nor $^3t^*$ is stable and both readily twist around their vinylene bond into the most stable triplet, an almost perpendicularly twisted triplet ($^3p^*$) shown in Figure 6A. $^3p^*$ is very close in energy to 0p and undergoes deactivation to $^0\alpha$ through intersystem crossing.¹²⁻¹⁴ Then, the resulting 0p collapses to either *cis* or *trans* isomers in the ground state at a certain ratio. Therefore, after irradiation for a sufficient time, the reaction results in a photostationary

state comprising a certain ratio of both isomers. The *cis* isomer content is more than the *trans* one in the photostationary state, because the $^3p^*$ lies close to the *cis* side. Figure 6A coincides with both the experimental results and quantum chemical calculations.^{11,15}

On the other hand, in the case of 9,10-bis(phenylthiovinylene)anthracene, the *cis* isomer was irreversibly isomerized to the *trans* isomer, since no reverse reaction from their *trans* to *cis* took place by the photoisomerization. It is considered that there is no participation of $^3p^*$ as an important intermediate, since it would give a mixture of both isomers. The authors have proposed a potential energy diagram depicted in Figure 6B based on the experimental results. Thus, $^3c^*$ resulting from excitation undergoes twisting around the vinylene bond to attain $^3t^*$ by passing through a perpendicular conformation. The excited state does not stay at the $^3p^*$ conformation for a sufficient lifetime to be deactivated to the ground state, and this conformation would be only a simple point to be quickly passed.^{13,14} Therefore, the excited state would undergo deactivation from $^3t^*$ to the ground state, instead of the decay from $^3p^*$ to the ground state. On recycling these processes, the irreversible isomerization takes place successively.

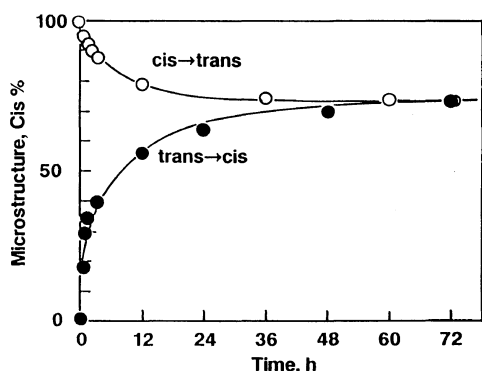


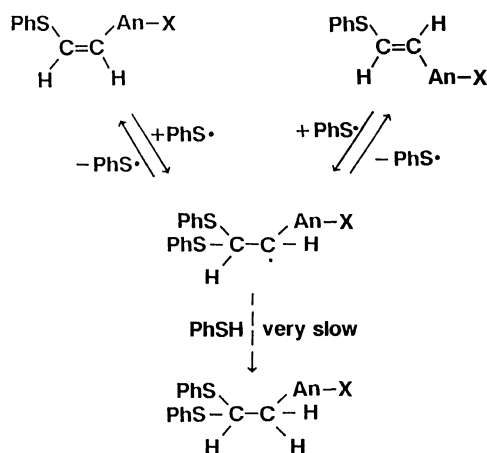
Figure 7. Isomerization of 9,10-bis(phenylthiovinylene)anthracene in the presence of thiophenol in THF at 50°C under nitrogen atmosphere: $[cis]_0 = [trans]_0 = 0.026 \text{ mol l}^{-1}$; $[thiophenol]_0 = 0.00026 \text{ mol l}^{-1}$ (IR method).

This dramatic feature of the isomerization of the model compound containing anthracene is considered due to the highly conjugated π system of anthracene linked to the vinylene unit.

Isomerization of Model Compound in the Presence of Radical

The model compound containing anthracene ring isomerizes easily from its *cis* isomer to the *trans* one in irreversible isomerization by UV irradiation just mentioned above. How does it occur in the presence of a radical source, such as thiophenol in the THF solution? In the presence of a small amount of thiophenol in a THF solution of the model compound, both the *cis* and *trans* isomers can undergo isomerization to the opposite configuration gradually. After reaction for a sufficient time, the reaction reaches an equilibrium state comprising a certain ratio of both isomers, in which the *cis* isomer contains 74%, much more than the *trans* one (Figure 7).

This thermal isomerization behavior compared to the UV-induced isomerization suggests that the thiol in the reaction solution acts as a catalyst to stimulate the isomerization on heating.¹⁶ This indicates that thiyl radicals are the active catalytic agents whose reversible addition and elimination to and from the



Scheme 3. Mechanism of isomerization in the presence of thiophenol.

vinylene unit may result in isomerization as shown in Scheme 3, where An-X means phenylthiovinyleneanthryl.

The absence of the methine and methylene absorption peaks at 2800 to 3000 cm^{-1} and other peaks different from the starting substrates and ^1H NMR spectra demonstrate that the catalysis of the isomerization by thiophenol could not bring about a saturated adduct formation. Even though the adduct is formed, the amount of it would be negligibly small. The reason would be due to the high degree of stability, *i.e.*, low reactivity of the intermediate carbon radical, in which the adjacent anthracene group stabilizes the methine radical to prevent the abstraction of the hydrogen from thiophenol forming a saturated adduct. Steric factors of the intermediate carbon radical may also affect the low rate of hydrogen abstraction from the thiol.

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