***cis* Addition Reaction of Thiophenol to Ethynylbenzene and Isomerization of Adduct as a Model of Poly(1,4-benzenedithiol-co-1,4-diethynylbenzene)**

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ABSTRACT: The mechanisms of *cis* polyaddition of 1,4-benzenedithiol to 1,4-diethynylbenzene were studied by means of a model reaction. As the model reaction, the addition reaction of thiophenol (TP) to ethynylbenzene (EB) was carried out in a NMR glass tube at 34°C under atmosphere of nitrogen and the reaction course was monitored by ¹H NMR method. Under an atmosphere of nitrogen an anti-Markownikoff type product, β -phenylthiostyrene, with 80% of the *cis* structure was obtained at various molar ratios of TP to EB. On the other hand, under an atmosphere of air, the addition reaction proceeded almost quantitatively for 4 h to form the anti-Markownikoff type adduct, which was initially rich in the *cis* structure, but *cis* content decreased gradually to below 50% even after the hundred conversion. In the case of the polyaddition of 1,4-benzenedithiol to 1,4-diethynylbenzene, high *cis* polymers were obtained initially both in solution and also in solid state polymerization. Consequently, the *cis* polymerization mechanism is the same as the *cis* adduct formation. MINDO/3 calculations with intermediates and products indicated that the *trans* adduct is more stable than the *cis* adduct, while the intermediate radical for the *cis* adduct (*cis**) is 3.4 kcal mol⁻¹ lower than that for the *trans* adduct (*trans**). Accordingly, the *cis* adduct and *cis* vinylene of the polymer are preferentially formed by kinetic control. The effects of oxygen, thiophenol, AIBN and reaction temperature on the isomerization of the *cis* to *trans* adduct were also studied by ¹H NMR method. It was found that the isomerization of the *cis* to *trans* adduct hardly occurred in the absence of oxygen, AIBN or phenylthio radical at 34°C.

KEY WORDS Thiophenol / Ethynylbenzene / 1,4-Benzenedithiol / 1,4-Diethynylbenzene / *cis* Addition / *cis* Addition Mechanism / Isomerization of *cis* Adduct / *cis* Polyaddition / MINDO / 3 /

The free radical addition reactions of thiols to acetylenes have been carried out under several conditions. In the case of aromatic acetylene, it was found that the addition reaction took place easily to yield 1,2-disubstituted ethenes in an anti-Markownikoff manner.¹⁻³ But, the *cis*-*trans* ratio of products was affected by reaction conditions such as temperature,^{4,5} atmosphere, time and a molar ratio of thiols to acetylenes.⁶

Oswald⁶ studied the addition reaction of thiophenol to ethynylbenzene at various molar ratios at 0°C with UV-irradiation for 2 h. It

was found that a high excess of ethynylbenzene over thiophenol (1.1:0.05) resulted in the formation of a high *cis* content mixture (more than 95%). However, a high excess of thiophenol over ethynylbenzene (0.05:1.0) resulted in the formation of a low *cis* content mixture (*ca.* 16%). These results do not clearly indicate whether the ratio of the *cis* and *trans* adducts is controlled by the molar ratio of ethynylbenzene and thiophenol or the *cis* adduct produced is isomerized to the *trans* adduct.

Previously, the authors reported the poly-

addition of 1,4-benzenedithiol to 1,4-diethynylbenzene in solution⁷ and also in solid state⁸ under UV-irradiation to yield the 1:1 polymer of 1,4-benzenedithiol with 1,4-diethynylbenzene.

The microstructures of polymers⁹ obtained in the solution polymerization were found to be mainly the *cis* structure, regardless of the polymerization temperature (0°C, *cis* 95%; 60°C, *cis* 88%). In the case of the solid state polymerization, polymers obtained were also the *cis* rich structure (0°C, *cis* 94%; 60°C, *cis* 81%; 80°C, *cis* 73%), and exhibited a high crystallinity.

This paper deals with the addition reaction of thiophenol (TP) to ethynylbenzene (EB) as a model reaction of the polyaddition, and the effects of reaction temperature, oxygen, TP, AIBN on the *cis*⇌*trans* adduct isomerization by means of the ¹H NMR method.

The results of the addition reaction of TP to EB are briefly discussed based on MINDO/3 calculations.

EXPERIMENTAL

Materials

Ethynylbenzene (EB)¹⁰ was prepared from 1,2-dibromoethylbenzene and redistilled over calcium hydride before use, bp 44–45°C/25 mmHg (bp 44°C/25 mmHg).¹⁰

Thiophenol (TP, Wako Pure Chem. Industries) was distilled before use, bp 71–72°C/15 mmHg (71°C/15 mmHg).¹¹ CCl₄ (Wako Pure Chem. Industries) was distilled before use. AIBN (Wako Pure Chem. Industries) was used as received.

Addition Reaction of TP to EB

cis- and *trans*-β-Phenylthiostyrenes were prepared by the previous method.¹² The *cis* adduct was recrystallized from heptane solu-

tion. The *trans* adduct was recrystallized from diethyl ether solution.¹³ The reagents were charged into a 5φ NMR sample tube by a medical syringe under an atmosphere of nitrogen, and then were sealed at dry ice/MeOH temperature. The addition reaction rate of TP to EB was measured at 34°C by JEOL PMX 60si ¹H NMR. On the other hand, under air, degassed CCl₄ was used as a solvent to control moderately the reaction rate. The extent of addition reaction of TP to EB was followed by determining the decrease of –C≡CH (s, δ 2.9 ppm), –SH (s, δ 3.1 ppm), and increase of CH=CH (AB quartet, δ 6.9–6.4 ppm) of β-phenylthiostyrene. The *cis*/*trans* isomer ratio of β-phenylthiostyrene in the reaction mixture was determined with the peak area ratio at the chemical shifts of *cis* (q, δ 7.3 ppm) and *trans* (q, δ 6.6 ppm) vinylic protons.

Isomerization of β-Phenylthiostyrene

The isomerization of β-phenylthiostyrenes with oxygen, thiophenol, and AIBN was carried out in CCl₄ solution. The *cis* or *trans*-β-phenylthiostyrene purified was charged into a 5φ NMR sample tube under nitrogen, and added distilled and degassed CCl₄ with semi-close system, which was carefully sealed. The rate of isomerization was measured by the ¹H NMR method.

Quantum Chemical Calculation

Quantum chemical calculations¹⁴ were performed on DEC-VAX 8350 computer using MINDO/3¹⁵ program.

RESULTS AND DISCUSSION

Previously, the authors reported the polyaddition of 1,4-benzenedithiol to 1,4-diethynylbenzene under UV-irradiation in toluene solution⁷ and in solid state.⁸ The microstructures of polymers obtained were found to be mainly the *cis* structure induced by the *trans* addition of thiol to ethynyl group.⁹

Addition Reaction of TP to EB

The kinetic study with the addition reaction of TP to EB was already investigated.¹⁶ As expected from the kinetic study, the yield of the product, β -phenylthiostyrene, increased with increasing EB in the feed molar ratio as shown in Figure 1a. The stereochemistry of the product was found to be 100–80% the *cis* structure regardless of the molar ratio of TP and EB (Figure 1b). *cis* Content was initially very high and decreased to 80%. This means that the product prefers the *cis* form by a kinetic controlled reaction.

On the other hand, the addition reaction of TP to EB progresses rapidly in CCl_4 solution at 34°C under atmosphere of air to give β -phenylthiostyrene, since oxygen in air acceler-

ates the addition reaction (Figure 2a). CCl_4 was used as a solvent to control the reaction rate and was convenient to measure ^1H NMR of the reaction mixture. However, the reproducibility of the time–yield curves was not good due to amount of oxygen in the reaction mixture. The *cis* content of the addition product was about 80% at the initial stage and then decreased (Figure 2b) even after the hundred conversion. In the case of EB/TP being 1/5, the *cis* content decreased to 25% for 4 h.

The elementary addition reaction of TP to EB has already been discussed by the authors.¹⁶ Oxygen, radical initiators, and UV-light initiate the thiophenyl radical forma-

Figure 1. Addition reaction of thiophenol to ethynylbenzene in bulk at 34°C under N_2 and darkness. EB:TP in molar ratio: $\square$, 5:1; $\blacksquare$, 2:1; $\circ$, 1:1; $\blacktriangle$, 1:2. a) Relation between reaction time and yield by NMR. b) Relation between reaction time and *cis* content by NMR.

Figure 2. Addition reaction of thiophenol to ethynylbenzene in CCl_4 at 34°C under air and darkness. EB:TP in molar ratio: $\square$, 5:1; $\blacksquare$, 2:1; $\circ$, 1:1; $\blacktriangle$, 1:2; $\triangle$, 1:5. $[\text{C}_6\text{H}_5\text{C}\equiv\text{CH} + \text{C}_6\text{H}_5\text{SH}] = 1.0 \text{ mol l}^{-1}$. a) Relation between reaction time and yield by NMR. b) Relation between reaction time and *cis* content by NMR.

Scheme 1.

tion. The rate determining step is the addition reaction of thiophenyl radical to EB.¹⁸ The intermediate carbon radical may be *cis** or *trans** configuration, as shown in Scheme 1.

The abstraction of hydrogen from TP by the radical (*cis** or *trans**) then takes place. The radical addition reaction of TP to EB in the liquid phase occurs predominantly by a *trans* addition mechanism and may yield the thermodynamically less favored *cis* vinylene-sulfide. Then, the isomerization of *cis* to *trans* adduct may take place by oxygen and/or TP. That is, the *trans* adduct is produced by a thermodynamically controlled reaction. These conclusions, however, are not compatible with the discussion of the controlling factors of the *cis* and *trans* isomer ratio based on the activation energy difference between the *cis* and *trans* intermediate carbon radicals by ESR.^{17,18}

The quantum chemical calculation may afford a better understanding the present experimental results. The apparent activation enthalpy of the intermediate carbon radical ($\Delta H_a^\ddagger$) and apparent enthalpy of the *cis* and *trans* adducts (ΔH_a) were calculated by the MINDO/3 method. The results are shown in Figure 3.

The apparent enthalpy of the *trans* adduct was 2.6 kcal mol⁻¹ lower than that of the *cis* adduct. However, the apparent activation enthalpy of the intermediate radical *cis** for the *cis* adduct was 3.4 kcal mol⁻¹ lower than that of the *trans* adduct. These results show that the stereochemistry of the radical addition reaction of TP to EB is determined by the kinetic process. Using the apparent activation

Figure 3. Relation between reaction coordinate and ΔH_a (by MINDO/3, Yoshida *et al.*¹⁴).

enthalpy difference $\Delta\Delta H_a^\ddagger$ between *cis** and *trans**, the ratio of *cis** may be calculated as more than 99%. This means that the addition reaction of TP to EB exclusively gives the *cis* adduct. The experimental results shown in Figure 1b at the initial state agree with the calculations. However, the experimental results suggest isomerization of the *cis* adduct to the *trans* one in the course of the reaction.

cis-trans Isomerization of β -Phenylthiostyrene

Under nitrogen, the effects of oxygen, thiophenol, thiophenol-AIBN, and temperature on the isomerization of β -phenylthiostyrenes were studied by the ¹H NMR method.

Effect of Oxygen

The effect of oxygen on the isomerization of the pure *cis* adduct to the *trans* adduct in the purified and degassed CCl₄ at 34°C under atmosphere of nitrogen is shown in Figure 4. The isomerization of the *cis* to the *trans* does not occur appreciably in the absence of added

Figure 4. Effect of oxygen on isomerization of *cis*- β -phenylthiostyrene in CCl_4 at 34°C under N_2 and darkness by NMR. $[\text{cis}]_0 = 0.67 \text{ mol l}^{-1}$.

Figure 5. Effect of thiophenol on isomerization of *cis*- β -phenylthiostyrene in CCl_4 at 34°C under N_2 and darkness by NMR. $[\text{cis}]_0 = 0.67 \text{ mol l}^{-1}$; $[\text{C}_6\text{H}_5\text{-SH}] = 0\text{--}0.13 \text{ mol l}^{-1}$.

oxygen.

However, the *cis* adduct isomerizes to the *trans* in the presence of added oxygen. For instance, in the presence of 1% oxygen in an atmosphere of nitrogen, the 100% *cis* adduct isomerized to 40% *cis* at 34°C for 12 h. The isomerization of the *cis* adduct to the *trans* one may be expressed as follows:

Effect of Thiophenol

The effect of thiophenol on the isomerization of the *cis* to the *trans* adduct was also examined without added oxygen (Figure 5). It was found that the isomerization of the *cis* to the *trans* adduct did not take place even in the presence of a large amount of thiophenol (20 mol% *vs.* the *cis* adduct). That is, the isomerization of the *cis* to *trans* adduct was not directly related to thiophenol itself.

Effect of Thiophenol and AIBN

In the presence of AIBN, isomerization of the *cis* to the *trans* adduct was induced under

Figure 6. Effect of AIBN and thiophenol on isomerization of *cis*- β -phenylthiostyrene in CCl_4 at 34°C under N_2 and darkness by NMR. $[\text{cis}]_0 = 0.67 \text{ mol l}^{-1}$; $[\text{AIBN}] = 0.013 \text{ mol l}^{-1}$; $[\text{C}_6\text{H}_5\text{-SH}] = 0.006 \text{ mol l}^{-1}$.

nitrogen as shown in Figure 6. Further, in the presence of thiophenol and AIBN, the isomerization of the *cis* to the *trans* adduct was accelerated. These results indicate that the isomerization of the *cis* to the *trans* adduct is induced by a radical such as oxygen or $(\text{CH}_3)_2\dot{\text{C}}\text{-CN}$ and is more conveniently accelerated by phenylthio radical ($\text{C}_6\text{H}_5\text{-}\dot{\text{S}}$) created from thiophenol. The isomerization mechanism in the course of the adduct synthesis may be expressed as follows:

Effect of Temperature

Figure 7 shows effect of temperature on the isomerization of the *cis* to the *trans* adduct in the purified and degassed CCl_4 under atmosphere of nitrogen. It was found that thermal effect is very efficient for the isomerization of the *cis* to the *trans* adduct. For instance, at 60°C for 40 min under nitrogen, the isomerization of purified *cis* adduct reached 84/16 in *cis/trans*. Activation energy for the isomerization of the *cis* to the *trans* was calculated, from plots of $\log(\text{initial rate of the isomerization})$ vs. $1/T$, as be about 14 kcal mol^{-1} .

trans-cis Isomerization of β -Phenylthiostyrene

The isomerization of the *trans* to the *cis* adduct was also attempted under several conditions. However, the isomerization of the *trans* to the *cis* adduct was not induced by oxygen, thiophenol-AIBN, and thermal conditions. It is confirmed experimentally that the *trans* isomer is thermodynamically much more stable than the *cis* isomer.

Accordingly, it is concluded that thiophenol adds to ethynylbenzene to form *cis*- β -phenylthiostyrene and the *cis* adduct isomerizes to the *trans* one by the aid of oxygen or radicals but not by thiophenol itself. These experimental results well coincide with the quantum chemical calculation by MINDO/3. Moreover, benzenedithiol added also to ethynylbenzene to give the *cis* adduct at 20°C under nitrogen.¹² The *cis* adduct isomerized to the *trans* one in the presence of excess benzenedithiol. That is, the *p*-substituent groups of thiophenol and ethynylbenzene did not affect the controlling factor of the *cis* and *trans* structure. So, the model addition reactions can be used as a

Figure 7. Effect of temperature on the isomerization of *cis*- β -phenylthiostyrene in CCl_4 under N_2 and darkness by NMR. $[\text{cis}]_0 = 0.67 \text{ mol l}^{-1}$.

reference of the *cis* polymerization reaction mechanism. Consequently, the *cis* structure of the polymer of 1,4-benzenedithiol with 1,4-diethynylbenzene may result mainly by kinetically controlled addition of the thiyl radical to the ethynyl bond.

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