Microstructure of an Addition Polymer Composed of 1,4-Benzenedithiol and 1,4-Diethynylbenzene

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(Received July 22, 1988)

ABSTRACT: The microstructures of addition polymers composed of 1,4-benzenedithiol (BDT) and 1,4-diethynylbenzene (DEB) were studied by IR method. As model compounds for the assignment of the IR spectra, the compound [A] *cis-cis* and the compound [B] *trans-trans* were used.

The characteristic absorption peak of the *cis*-linkage of the model compounds was assigned to be 1350 cm^{-1} (ϵ in $1\text{ mol}^{-1}\text{ cm}^{-1}$; 122.1 in CCl_4) and that of the *trans*-linkage was 940 cm^{-1} (ϵ in $1\text{ mol}^{-1}\text{ cm}^{-1}$; 311.6 in CCl_4) in the IR spectra. The microstructures of the polymers were quantitatively estimated by the following equations.

$$C_{\text{cis}} = 7.80 \times 10^{-3} D_{1350} - 2.10 \times 10^{-4} D_{940}$$

and

$$C_{\text{trans}} = 3.20 \times 10^{-3} D_{940} - 3.21 \times 10^{-4} D_{1350}$$

where C_{cis} and C_{trans} mean the concentrations of the *cis*- and the *trans*-linkage in the polymers, and D_{1350} and D_{940} are the absorbances of the *cis*-linkage at 1350 cm^{-1} and the *trans*-linkage at 940 cm^{-1} , respectively. The microstructures of polymers obtained in the toluene solution under UV-irradiation were found to be mainly the *cis*-structure, regardless of the polymerization temperature (0°C , *cis* 95%; 60°C , *cis* 88%). However, the *cis*-contents of the polymers obtained in solid state under UV-irradiation decreased with increasing polymerization temperature (0°C , *cis* 94%; 60°C , *cis* 81%; 80°C , *cis* 73%). The polymerization mechanism in the solid state may differ from that in solution. The arrangement and mobility of the reacting molecules in the crystalline solid probably affect the opening mode of the acetylenic triple bond. These phenomena are briefly discussed.

KEY WORDS Microstructure of Addition Polymer / 1,4-Benzenedithiol / 1,4-Diethynylbenzene / Solid State Polymerization / Solution Polymerization / IR Spectrum / *cis*-Linkage / *trans*-Linkage / Model Compounds / *cis-trans* Isomerization /

Free-radical addition reaction of thiols to monosubstituted acetylene has been known for more than 50 years¹ and occurs in an anti-Markownikoff manner.² However, the addition polymerization of a dithiol to a com-

pound having one or two ethynyl groups has scarcely been known except the case for the addition polymerization of hydrogen sulfide to acetylene³ and the addition polymerization of 1,2-ethanedithiol or 1,6-hexanedithiol to 1,4-

bis(acetylenic keto)benzene.⁴ In the former case, hydrogen sulfide and acetylene were irradiated with a low pressure mercury lamp and the $\text{HS}\cdot$ radical produced in the direct photolysis was added to acetylene to form the radical, $\text{HSCHCH}\cdot$. Ethenethiol was produced by the abstraction of hydrogen from hydrogen sulfide. Consequently, a rapid polymerization of ethenethiol occurred and gave the polymer having the general formula $(\text{C}_2\text{H}_4\text{S})_n$. In the latter case,⁴ the addition polymerization was also found to proceed rapidly. Although the *cis*-configuration of the enonesulfide is assumed to form as below, the exact configuration of the repeat unit has not yet been determined.

Previously, the authors reported the addition polymerization of 1,4-benzenedithiol to 1,4-diethynylbenzene in the solution⁵ and also in the solid state.⁶ In the solid state polymerization the polymer obtained exhibits high crystallinity. The crystallinity was affected by photo-irradiation.⁷ For instance, in the region from 500 to 600 nm there are three characteristic wavelengths of 545.6, 567.8, and 590.1 nm. The irradiation at these lights in-

creases the crystallinity of the polymers. On the other hand, the photo-light of 501.1, 539.6, and 588.1 nm decreases steeply the peak intensity of the diffractions in the X-ray diagram. According to a preliminary investigation the present polymer possesses a layer structure with an orthorombic lattice.⁸ The peak intensity in the X-ray diagram seems to be associated with the amount of the layer structure. The *cis-trans* isomerization in the polymer molecules by photo-irradiation may affect the stability of the layer structure.

This report deals with the microstructure of the addition polymers composed of 1,4-benzenedithiol and 1,4-diethynylbenzene, and briefly discusses the relation between the microstructure and layer structure of polymers.

EXPERIMENTAL

1,4-Benzenedithiol (BDT) and 1,4-Diethynylbenzene (DEB)

BDT and DEB were prepared by the previous method.⁶ BDT was recrystallized from *n*-hexane solution, and then sublimed at 70°C under reduced pressure prior to use. DEB was purified by recrystallization from *n*-hexane solution, and then sublimed at 60°C under reduced pressure prior to use.

Model Compounds

The model compounds for assignments of the IR spectrum of polymers were synthesized by the previous method.⁹

Solution and Solid State Polymerization

The solution⁵ and solid state⁶ polymerizations were carried out as previously re-

ported. The photo-irradiation polymerizations were carried out by high pressure mercury lamp of 450 W (USHIO).

Measurement

Model compounds ([A],[B]) were analyzed by $^1\text{H-NMR}$ (JEOL JNM-FX 270) and IR (Hitachi 260-50 and Hitachi EPI-S2). UV spectra and DSC of the model compounds were measured by a Shimadzu UV-260 and a Rigaku TAS-100, respectively.

The characteristic absorption peaks and their extinction coefficients (ϵ) of the *cis*- and the *trans*-compounds were determined by the

IR method in a solution such as that of CCl_4 or CS_2 .

RESULTS AND DISCUSSION

Previously, the authors reported the addition polymerization of BDT to DEB under UV-irradiation in toluene solution⁵ and in the solid state.⁶ The reaction scheme is as follows.

The polymer structure coincides with the IR spectrum of polymers taken with the KBr disk method. However, the configuration of the vinylene group had not yet been determined. The model compounds are useful for assignment of the microstructures of polymers.

Model Compounds [A] and [B]

$^1\text{H-NMR}$ spectra of [A] and [B] are shown in Figure 1. Fourteen protons on the aromatic rings of the compound [A] appear in the range of δ 7.1 to 7.5, and four protons of the vinylene group are centered at δ 6.53 and 6.37 as the AB quartet type. The coupling constant of the vinylene protons $J_{\text{CH}=\text{CH}}$ is 10.5 Hz indicating the *cis*-linkage. On the other hand, the fourteen protons on the aromatic rings of the compound [B] are located in the range of δ 7.2 to 7.5. The chemical shift values for the four protons of the vinylene group are δ 6.88 and 6.67 as also for the AB quartet type. The coupling constant $J_{\text{CH}=\text{CH}}$ is 15.5 Hz suggesting the *trans*-linkage of the compound [B]. These assignments are consistent with the $^1\text{H-NMR}$ data taken with the *cis*-adduct (10.5 Hz) and *trans*-adduct (15.5 Hz) of thiophenol and phenylacetylene.¹⁰

Figure 2 shows the IR spectra of [A] and [B]. The $-\text{CH}=\text{CH}-$ stretching vibrations of aromatic rings and methyne groups appear at 3,075, 3,025 cm^{-1} . The $\text{C}=\text{C}$ skeletal stretching mode, the $-\text{CH}=\text{CH}-$ in-plane and the $-\text{CH}=\text{CH}-$ out-

of-plane vibrations of aromatic rings can be found at 1,600–1,450 cm^{-1} , 1,250–1,000 cm^{-1} , and 850–650 cm^{-1} , respectively. Generally, the vibrations of the symmetrically disubstituted *trans*-ethylenes appear at wave numbers between 970 and 930 cm^{-1} ,^{11a} but the $-\text{CH}=\text{CH}-$ out-of-plane deformation vibration of the *cis*-adducts cannot easily be assigned because of overlapping with the $-\text{CH}=\text{CH}-$ deformation vibrations of the aromatics and vinylene of the *cis*-adduct.^{11b} However, as shown in Figure 2(a) and (b), the characteristic absorption peak of the $-\text{CH}=\text{CH}-$ out-of-plane deformation vibration of the [A] *cis-cis* adduct can be assigned at 1,350 cm^{-1} and that of the [B] *trans-trans* adduct, at 940 cm^{-1} . The characteristic absorption peak at 1,350 cm^{-1} is recognized in the *cis*-adduct prepared from TP and PA, and similarly the absorption at 940 cm^{-1} is recognized with the *trans*-adduct of TP and PA. Therefore, the bands at 1,350 and 940 cm^{-1} can be ascribed to the characteristic modes for the *cis*- and *trans*-linkage, respectively.

Table I summarizes the spectroscopic data with the UV spectrum and the IR spectrum of the model compounds.

The extinction coefficient (ϵ) of the *cis-cis* adduct at 1,350 cm^{-1} is 122.1 ($\text{l mol}^{-1} \text{cm}^{-1}$) in the CCl_4 solution and 126.9 in the CS_2 solution at 23°C. Similarly, the ϵ of the *trans-trans* adduct at 940 cm^{-1} is 311.6 (l mol^{-1}

Figure 1. ^1H NMR spectra of model compounds in CDCl_3 at 35°C (TMS standard): (a) [A], *cis-cis* form

Figure 2. IR spectra of model compounds in CCl_4 at 23°C (Hitachi EPI-S2): (a) [A], *cis-cis* form $\text{C}_6\text{H}_5\text{-CH=CH-S-C}_6\text{H}_4\text{-S-CH=CH-C}_6\text{H}_5$; (b) [B], *trans-trans* form $\text{C}_6\text{H}_5\text{-S-CH=CH-C}_6\text{H}_4\text{-CH=CH-S-C}_6\text{H}_5$.

cm^{-1}) in the CCl_4 solution and 355.7 in the CS_2 solution at 23°C . However, the ϵ values of the *cis*- and *trans*-linkage of polymers cannot be directly determined because of the insolubility of polymers in conventional organic solvents. Accordingly, the ϵ values used for the microstructure analysis of polymers are tentatively selected to be the average values of the of [A] or [B] in CCl_4 and in CS_2 . Under this assumption the relation between the concentration of the *cis*-structure (C_{cis}) and the *trans*-one (C_{trans}) in the mixture of the *cis-cis* adduct and the *trans-trans* adduct is determined by the following equations, where D_{1350} and D_{940} mean the absorbances at 1,350 and 940 cm^{-1} , respectively.

Table I. Spectroscopic data of model compounds

	$\text{C}_6\text{H}_5\text{—CH=CH—S—C}_6\text{H}_5$ ⁹ <i>cis</i> <i>trans</i>		[A] ⁹ <i>cis-cis</i>	[B] ⁹ <i>trans-trans</i>
mp ^a (°C)	48.8—49.2 (44—46 ¹²)	38.6—39.5 (35—36 ¹⁰)	130.5—131.0	122.7—123.0
UV-spectrum at 22°C ^b				
λ _{max} (nm)	295.7 (296 ¹⁰)	306.9 (304 ¹⁰)	312.4	343.5
ε (l mol ⁻¹ cm ⁻¹)	21,000 (19,000 ¹⁰)	20,000 (20,000 ¹⁰)	48,000	44,000
IR-spectrum at 23°C				
Wave number (cm ⁻¹)	1,350	940	1,350	940
ε (l mol ⁻¹ cm ⁻¹)				
CCl ₄	55.7	147.2	122.1	311.6
CS ₂	55.9	157.8	126.9	355.7

^a Determined by DSC.^b Measured in hexane solution.

$$C_{cis} = 7.80 \times 10^{-3} D_{1350} - 2.10 \times 10^{-4} D_{940}$$

$$C_{trans} = 3.20 \times 10^{-3} D_{940} - 3.21 \times 10^{-4} D_{1350}$$

$$cis(\%) = C_{cis} / (C_{cis} + C_{trans}) \times 100$$

$$trans(\%) = C_{trans} / (C_{cis} + C_{trans}) \times 100$$

These equations can be used for estimation of the microstructures of polymers. However, it is noticed that the microstructures of polymers evaluated by this method may have error, since the extinction coefficients of polymers are not only assumed to be the same as those of model compounds [A] and [B], but also the IR spectra of polymers were measured by the KBr method.

Microstructure of Polymers

Figure 3 shows the IR spectrum of polymer obtained by the solid state polymerization. The characteristic absorption peaks of the *cis*- and *trans*-linkage appear at 1,350 and at 940 cm⁻¹. Using the above equations the microstructure of the polymer is estimated to be that the *cis* content is 72% and the *trans* one is 28%.

Table II shows the effect of the polymerization temperature and that of the initiation mode on the microstructure of polymers ob-

Figure 3. IR spectrum of a polymer obtained in solid state polymerization at 60°C under UV-irradiation by a high pressure mercury lamp of 450 W (Hitachi 260-50, KBr method).

tained by solution polymerization.

In the case of UV-irradiation polymerization, the microstructures of polymers were found to be mainly *cis*-structures regardless of polymerization temperature, but the *cis*-content in the polymers slightly decreases with increasing the polymerization temperature. The initiation modes such as UV, AIBN, and BPO have little effect on the content of the *cis*-linkage. The *cis*-structure was favored in the solution polymerization. On the other hand, the *cis*-content in polymers decreases with increasing polymerization temperature in solid

Table II. Effects of polymerization temperature and initiation mode on microstructures of polymers obtained by solution polymerization in toluene

No.	Polymn. temp	Polymn. time	Initiation mode ^a	Yield	<i>cis/trans</i> ^b
	°C	min		%	
1	0	10	UV	31.7	95/5
2	0	40	UV	59.7	99/1
3	30	10	UV	42.5	94/6
4	30	30	UV	66.1	91/9
5	30	30	AIBN	20.5	90/10
6	30	30	BPO	22.6	94/6
7	60	10	UV	61.7	88/12
8	60	10	AIBN	58.7	92/8
9	60	10	BPO	53.9	94/6
(Average value)					93/7

[BDT]=[DEB]=0.4 mol l⁻¹ in toluene.^a UV, high pressure mercury lamp of 450 W; [AIBN]=[BPO], 1/100 mol% for monomer concentration.^b Hitachi 260-50, KBr method.**Table III.** Effect of polymerization temperature on microstructures of polymers obtained by solid state polymerization under UV-irradiation^a

No.	Polymn. temp	Polymn. time	Yield	<i>cis/trans</i> ^b
	°C	min	%	
1	0	15	28	94/6
2	0	40	54	89/11
3	30	15	72	87/13
4	30	40	85	87/13
5	60	5	78	82/18
6	60	10	87	81/19
7	80	3	89	74/26
8	80	10	98	73/27

Sublimation conditions of monomers on a glass plate: 60°C, 5 min, 0.5 mmHg; cooling water, 9.8–10.9°C.

^a High pressure mercury lamp of 450 W.^b Hitachi 260-50, KBr method.

state polymerization as shown in Table III.

These differences in the *cis*-content in polymers obtained in the solution polymerization and in the solid state polymerization may depend on the polymerization mechanism, since a high stability of the intermediate radical in the solid state possibly induces the *cis-trans* isomerization of the carbon-carbon double bond as below or a relative arrangement and

the mobility of reacting molecules in the monomer crystals may affect the opening mode of the acetylenic triple bond.

A configurational change by the *cis-trans* isomerization of the vinylene group of polymers may also occur during solid state polymerization. In fact, when the No. 2 sample in Table II (*cis*-content 99%) is irradiated with the UV light from the high pressure mercury lamp for 5 hr at 60°C, the *cis*-content in polymers decreases about 20%. The *cis*-content of the polymer obtained in the solid state polymerization decreased also from 82% of *cis* to 71% under thermal treatment at 95°C for 1 hr under nitrogen atmosphere. However, the microstructures of polymers hardly changed at 70°C. That is, the *cis-trans* isomerization of a polymer is induced by the photo-irradiation

or by thermal treatment above 95°C. Consequently, the effect of isomerization on the *cis*-content in the resultant polymer is not so important within a short polymerization time. The crystallinity of polymers obtained in the solid state polymerization also slightly decreases with increasing polymerization temperature. That is, the decrease of the *cis*-content in polymers seems to induce decrease of crystallinity of polymers by destruction of the layer structures of polymers. This will be discussed later.

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