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Molecular Vibrations and Structures of Polyalkyl Polysulfides. II. Polyethylene Disulfide

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The polarized infrared spectra of oriented sheets of polyethylene disulfide were measured in the 4000—200 cm^{-1} region; the fiber period was thus found to be 8.8 Å by X-ray diffraction. It is found that this polymer does not have twofold symmetry axes intersecting the helical axis at right angles. The infrared-active normal vibrations of the four likely structural models were calculated by the use of a modified Urey-Bradley force field. The structure of polyethylene disulfide was concluded to be the GGG'G conformation along the sequence of the –S–CH$_2$–CH$_2$–S–S– bonds of the 3_1 helical model. This model is very similar to the structure of polymethylene disulfide reported in the previous paper. The above structure was then discussed in comparison with two models proposed previously (J. R. Katz, *Trans. Faraday Soc.*, **32**, 77 (1936); Y. Minoura, *J. Soc. Rubber Ind. Japan*, **28**, 399 (1955)).

In the previous paper,[1] we have reported on the molecular vibrations and the structure of polymethylene disulfide. As a continuation of the researches, we will deal with the molecular vibrations and the structure of polyethylene disulfide in the present paper. This is the second of a series of papers on polyalkyl polysulfides.

For polyethylene disulfide, Katz[2] reported the results of X-ray studies and proposed a structural model. Minoura,[3] in discussing the structure of this substance, found that the structural model proposed by Katz is not unique, but that several different structural models possibly have the measured fiber period.

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[1] M. Hayashi, T. Shiro and H. Murata, This Bulletin, **39**, 1857 (1966).

[2] J. R. Katz, *Trans. Faraday Soc.*, **32**, 77 (1936).

[3] Y. Minoura, *J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zassi)*, **73**, 244 (1952); **75**, 869 (1954); *J. Soc. Rubber Ind. Japan*, **28**, 399 (1955).

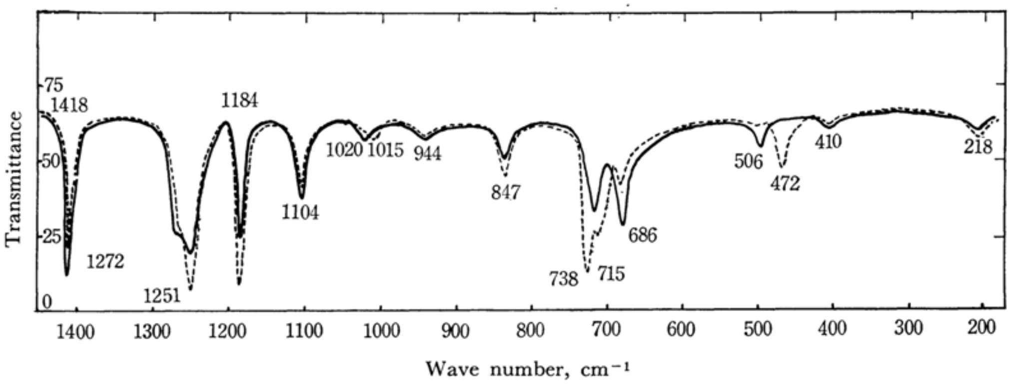

Fig. 1. Polarized infrared spectra of oriented film of polyethylene disulfide. The solid curve was measured with the electric vector perpendicular and the broken curve with the electric vector parallel to the direction of orientation.

We have measured the polarized infrared spectra of oriented sheets and have also remeasured the fiber period by X-ray diffraction. The infrared-active normal vibrations were calculated by the use of a modified Urey-Bradley force field, with the force constants transferred from the set obtained for simpler molecules with similar structures.[4]

Experimental

The sample used for the measurements was prepared by the reaction of 1, 2-dichloroethane and an aqueous solution of sodium disulfide, using magnesium hydroxide as an emulsifying agent. About a three-fold excess of sodium disulfide was used in order to obtain high-molecular-weight samples. The products were purified by continuous extraction with absolute alcohol; impurities and lower-molecular-weight polymers were thus washed out. The sheets were prepared by hot pressing and were subsequently uniaxially-oriented. The fiber period of the sample was measured as 8.8 Å on the X-ray rotation photograph; this value is in good agreement with the value reported previously.[2] The orientation of the solid sheets was not high enough for us to obtain more detailed information from the X-ray studies. The polarized infrared spectra of the oriented sheet were measured by a Perkin-Elmer 12C spectrometer; the results are shown in Fig. 1.

Discussion

There are four internal rotation angles per chemical unit of polyethylene disulfide $[-CH_2CH_2-SS-]_n$; one around the C–C bond, one around the S–S bond, and two around the two C–S bonds. As was described in the first paper of this series, the set of those four angles is sufficient to enable us to specify the structure of the entire helical polymer. As evidenced by the experimental data for simpler molecules,[5] there are three possible internal rotaion conformations around the C–C bond or the two C–S bonds, namely, the trans (180°) and the two gauche conformations (±60°), while the internal rotation angle around the S–S bond will be around 90°.

As in the previous paper, we will hereafter denote the structural models. For example, GTG′G is the structural model which consists of the gauche (60°), the trans (180°), the gauche prime (−60°) and the gauche (90°) internal rotation conformations along the sequence of the $-S-CH_2-CH_2-S-S-$ bonds. The angle around the S–S bond was fixed at 90° throughout the treatment.

As for molecular vibrations, it may be expected that, in general, there are twenty-two infrared active vibrations belonging to the A species. If the structural model has twofold symmetry axes intersecting the helical axis at right angles, these A vibrations can be classified into two groups (A_1 and A_2 species). We may expect a parallel dichroism for those vibrations, although the vibrations belonging to the A_1 species are infrared-inactive.

We have twenty-three pairs of degenerate vibrations belonging to the E species which exhibit a perpendicular dichroism. For 2_1 helical models, there are twenty-two B vibrations (with the phase difference of 180°) which give rise to perpendicular bands.

As for the S–S stretching mode, there is one A vibration and one pair of E vibrations. If twofold symmetry axes exist, the A vibration belongs to the A_1 species and, hence, becomes infrared-inactive. From the experimental data for such simpler molecules as dimethyl disulfide, we would expect, in the 500 cm^{-1} region, the bands due to

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[4] M. Hayashi, Y. Shiro, T. Oshima and H. Murata, This Bulletin, **38**, 1734 (1965); M, Hayashi, Y. Shiro, M. Murakami and H. Murata, ibid., **38**, 1740 (1965); M. Hayashi, Y. Shiro and H. Murata, ibid., **39**, 118 (1966).

[5] E. Hirota, ibid., **31**, 130 (1958); M. Hayashi, *J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zassi)*, **78**, 101 (1958); M. Hayashi, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **26**, 608 (1957).

TABLE I. STRUCTURAL MODELS OF POLYETHYLENE DISULFIDE WITHOUT TWOFOLD SYMMETRY AXES INTERSECTING THE HELICAL AXIS AT THE RIGHT ANGLES

Model	Internal rotation axes*				Expected fiber period (Å)	m_n**
	S–C	C–C	C–S	S–S		
TTGG	T	T	G	G	8.8	2_1
TGGG	T	G	G	G	8.8	3_1
TG′G′G	T	G′	G′	G	6.5	3_1
TG′GG	T	G′	G	G	6.6	3_1
GTG′G	G	T	G′	G	8.8	4_1
GGG′G	G	G	G′	G	8.8	3_1
GG′G′G	G	G′	G′	G	2.0	2_1

* T, G and G′ mean the internal rotation angles of 180°, 60° and −60°, respectively except for the angles around the S–S bond which are 90°.

** m: the number of repeating units per fiber period.
n: the number of helical turns per fiber period.

TABLE II. THE FORCE CONSTANTS ($F'=-0.1F$)

		(md./Å)			
K(C–H)	4.329	H(CSS)	0.15	F(CSS)	0.25
K(C–S)	1.8	H(HCS)	0.294	F(CSS)	0.192
K(S–S)	2.37	H(HCH)	0.331	F(HCH)	0.2
K(C–C)	2.2	H(CCS)	0.052	F(CCS)	0.056
P(CH)	−0.13	H(HCC)	0.156	F(HCC)	0.459
		(md. Å)			
Y(CS)	0.052	Y(SS)	0.147	Y(CC)	0.15
κ(CH_2)	0.058	l(CH_2)	0.057	t	0.136
g	−0.051				

P: CH bond stretching interaction constant.
l: angle interaction constants of CH_2 group.
Y: torsion constants.
t, g: trans and gauche angle interaction constants for the CH_2–CH_2 groups.

the S–S stretching modes, but no other bands. As is shown in Fig. 1 and Table III, we have observed two infrared bands, at 506 and 472 cm^{-1}, which exhibit a perpendicular and a parallel dichroism respectively. This indicates that the molecular conformation of this substance does not have twofold symmetry axes intersecting the helical axis at right angles.

In Table I, we have listed seven possible structural models (without twofold symmetry axes) and the expected fiber periods. Of these structural models, we may discard two of them (TG′G′G and TG′GG) since their expected fiber periods are quite different from the observed values. The GG′G′G conformation is not a likely model either, since, for this conformation, the steric hindrance is very large.

Four structural models (TTGG, TGGG, GTG′G and GGG′G) remain as the 2_1, 3_1, 4_1 and 3_1 helical conformations respectively. The values of internal rotation angles were calculated so as to reproduce the measured fiber periods.

By the use of the bond length values of r(S–S)=2.08 Å, r(C–S)=1.81 Å, and r(C–C)=1.54 Å, and the valency angles of α(CSS)=105° and α(SCC)=112°, the sets of internal rotation angles, (165°, 170°, 52.6°, 90°), (166°, 63°, 52°, 90°), (73°, 196°, −73°, 90°) and (71°, 68,° −71°, 90°) were obtained for TTGG, TGGG GTG′G and GGG′G respectively. The first two structural models have trans and gauche C–S bonds, but the last two have gauche and gauche prime C–S bonds. As for the C–C bond, the first and third model are in the trans form, while the second and last are in the gauche form.

It is well-known that the CH_2 rocking frequencies of the -CH_2CH_2- groups exhibit frequency differences characteristic of the conformation around the C–C bond. For example, in the case of 1, 2-dithiamethyl ethane, the frequency differences for the trans and gauche isomers are found to be 271 cm^{-1} and 118 cm^{-1} respectively. The difference for the trans isomer is always found to be much larger than for the gauche isomer.

For polyethylene disulfide, we may expect four infrared bands due to the CH_2 rocking modes, that is, two parallel bands belonging to the A species and two perpendicular bands belonging to the E species. Judging from the results of the normal vibration calculation, the bands belonging to the E species are possibly overlapped with the bands belonging to the A species for any

TABLE III. OBSERVED AND CALCULATED FREQUENCIES OF POLYETHYLENE DISULFIDE (cm^{-1})

Observed[*1]	A species Calculated				Assignment[*3]
	TTGG[*2]	TGGG[*2]	GTG'G[*2]	GGG'G[*2]	
2980 s	2975	2972	2975	2972	CH str.
2980 s	2964	2968	2964	2967	CH str.
2920 vs	2929	2925	2929	2925	CH str.
2920 vs	2908	2911	2908	2911	CH str.
1418 s	1427	1427	1428	1427	CH_2 scissor.
1418 s	1424	1426	1424	1426	CH_2 scissor.
1272 s	1287	1301	1287	1301	CH_2 wag. (83), CH_2 scissor. (13)
1251 vs	1286	1290	1286	1291	CH_2 wag. (63), CH_2 twist. (22)
1184 s	1196	1168	1195	1167	CH_2 twist. (67), CH_2 wag. (12)
1104 m	1160	1139	1160	1140	CH_2 twist. (75), CH_2 wag. (12)
1015 w //	1038	1035	1042	1029	CC str. (54), CH_2 rock. (28)
944 vw	988	955	978	950	CH_2 rock. (63), CC str. (18)
847 m	733	868	721	872	CH_2 rock. (73), CH_2 wag. (11)
738 s //	702	664	715	666	CS asym. str.
686 m	691	641	692	646	CS sym. str.
472 m //	515	508	458	475	SS str.
410 vw	351	404	337	398	SCC asym. def. (62), CH_2 rock. (17)
	255	343	297	290	CCS asym. def. (36), CC torsion (28)
218 w	182	191	217	245	CSS syn. def. (69), CC torsion (10)
	113	147	163	193	CC torsion (47), CSS asym. def. (30)
	94	118	61	50	SS torsion (47), CC torsion (14)
	64	84	52	27	CS torsion

Observed[*1]	Calculated				Assignment[*3]
	B species		E species		
	TTGG[*2]	TGGG[*2]	GTG'G[*2]	GGG'G[*2]	
2980 s	2975	2971	2975	2971	CH str.
2980 s	2963	2965	2964	2966	CH str.
2920 vs	2929	2919	2929	2918	CH str.
2920 vs	2908	2908	2909	2909	CH str.
1418 s	1427	1428	1428	1427	CH_2 scissor.
1418 s	1424	1427	1424	1426	CH_2 scissor.
1272 s	1287	1300	1288	1300	CH_2 wag. (85), CH_2 scissor. (11)
1251 vs	1286	1294	1285	1295	CH_2 wag. (66), CH_2 twist. (14)
1184 s	1196	1169	1198	1168	CH_2 twist. (63), CH_2 wag. (21)
1104 m	1160	1138	1164	1139	CH_2 twist. (78), CH_2 wag. (13)
1020 w ∠	1038	1032	1043	1032	CC str. (56), CH_2 rock. (31)
944 vw	986	960	981	963	CH_2 rock. (65), CC str. (14)
847 m	735	869	721	870	CH_2 rock. (78)
715 sh ∠	703	667	718	668	CS asym. str.
686 m	694	640	696	642	CS sym. str.
506 w ∠	514	520	482	495	SS str. (92)
410 vw	319	420	351	420	SCC asym. def. (58), CSS sym. def. (10)
	263	326	279	278	CCS asym. def. (31), CC torsion (18)
218 w	195	208	242	218	CSS def. (53), SS torsion (10)
	174	195	151	140	CC torsion (30), SS torsion (18)
	107	106	93	85	SS torsion (58), CC torsion (23)
	79	43	72	60	CS torsion (41), SS torsion (10)
	—[*4]	29	43	18	CS torsion (53), SS torsion (15)

[*1] The dichroism is shown as // and ∠ only for the infrared bands which exhibit clearly.

[*2] The helical models are 2_1 for TTGG, 3_1 for TGGG and GGG'G.

[*3] Diagonal elements of potential energy distributions of the structural model GGG'G are added in parentheses for mixed vibrrations. (%)

[*4] This frequency is not existing since the phase difference is 180° for this model.

structural models, so that the dichroism of the band may not be expected to be high for the CH_2 rocking bands. In the region from 1050 to 700 cm^{-1}, we have observed seven infrared bands, at 1020, 1015, 944, 847, 738, 715 and 680 cm^{-1}. In the higher-frequency part of the region, we may also expect C–C stretching frequencies, while in the lower-frequency part of the region, we may also expect C–S stretching frequencies. Since we found C–C stretching frequncies around 1020 cm^{-1} for simpler molecules, such as 1, 2-ethanedithiol and 1, 2-dithiamethyl ethane, we may possibly assign the bands at 1020 and 1015 cm^{-1} to the C–C stretching frequencies. The band at 1020 cm^{-1} exhibits a highly perpendicular dichroism and so is assigned to the E species, whereas the band at 1015 cm^{-1} exhibits a highly parallel dichroism and is assigned to the A species.

We assign the band at 680 cm^{-1} to one of the C–S stretching frequencies, since this frequency is too low for the CH_2 rocking frequencies in comparison with the assignments given to simpler molecules. Since in no case are the C–S stretching frequencies higher than 750 cm^{-1}, we may assign the bands at 738 and 715 cm^{-1} to the C–S stretching frequencies also. We may assign the bands at 944 and 847 cm^{-1} to the overlapped CH_2 rocking frequencies. Their frequency difference is as great as 97 cm^{-1}, which is nearly equal to that for the gauche isomer of 1, 2-dithiamethyl ethane, This indicates that the conformation around the C–C bond of polyethylene disulfide is gauche; hence, the structural models TTGG and GTG′G may be eliminated from consideration.

We have calculated the infrared-active normal vibrations in order to confirm the assignments of the observed infrared bands, and also in order to examine which structural model is preferable, TGGG or GGG′G.

For the calculation of the inverse kinetic energy matrix, the bond length of $r(\text{C–H})=109$ Å and the valency angle of $\alpha(\text{HCH})=109°28'$ were used, besides the molecular parameters described above for TTGG, TGGG, GTG′G and GGG′G structural models. For the potential energy matrix, a modified Urey-Bradley force field was used. This force field includes the same modifications as were used for such simpler molecules as 1, 2-ethanedithiol and 1, 2-dithiamethyl ethane.$^{4)}$ These modifications are: (1) torsional terms with the force constants Y, (2) C–H bond interaction terms with the force constants p, (3) angle interaction terms between the angles of one CH_2 group with the force constants, l, and (4) angle interaction terms between the angles of the CH_2–CH_2 group with the force constants t and g, which are usually called the trans and the gauche interaction terms.

The force constants were all transferred from the set obtained for simpler molecules. They are listed in Table II, while results are shown in Table III. The method developed by Miyazawa et al.$^{6)}$ was used in the calculations.

First, from the calculation, it was found that the frequencies of the A and E vibrations due to the common vibrational modes, nearly coinciding except for the S–S stretching mode, some of the skeletal bending modes, and some of the torsional modes. Second, the calculated frequencies above 1000 cm^{-1} are not appreciably affected by the structural models, and the agreements between the observed and calculated frequencies are satisfactory for all structural models in this region. Third, the frequency differences of the two CH_2 rocking vibrations belonging to the same species exhibit behavior similar to that of simpler molecules; the trans conformation around the C–C bond produces a much larger frequency difference than that for the gauche conformation. From this reason too, as we have described before, we may discard the TTGG and GTG′G structural models from consideration.

Fourth, we found an appreciable frequency difference in the S–S stretching vibrations belonging to the A and E species for GTG′G and GGG′G, while the difference is very small for TTGG and TGGG. The observed S–S stretching frequencies and the difference in their A and E vibrations agree with the calculated frequencies of GTG′G and GGG′G much better than do the other models.

Furthermore, we found that the difference in the observed and the calculated frequencies of the CCS deformation vibration is much larger for the trans conformation of the C–C bond than that for the gauche conformation.

Therefore, we may conclude that the conformations of the $-S-CH_2-CH_2-S-S-$ bond sequence are gauche, gacuhe, gauche prime and gauche; that is, the structural model of polyethylene disulfide is most probably the 3_1 helical model of the GGG’G type.

It may be seen in Table III that the calculated frequencies of two C–S stretching vibrations of both the A and E species do not agree very well with the observed frequencies. However, in previous papers on the vibrational assignments of such simpler molecules as 1, 2-dithiamethyl ethane, we have already pointed out that the calculated frequency differences of the two C–S stretching vibrations are much smaller than those of the observed values. We have concluded that this is due to imperfections in the force field; we therefore wish to modify the force field if sufficient observed data become available. In polyethylene disulfide

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6) T. Miyazawa, *J. Chem. Phys.*, **35**, 693 (1961); *J. Polymer Sci.*, **55**, 214 (1961); T. Miyazawa, K. Fukushima and Y. Ideguchi, *J. Chem. Phys.*, **37**, 764 (1962); ibid., **38**, 2709 (1963).

also, we see a similar situation. The assignments of the observed infrared bands are shown in Table III, together with the potential energy distributions.

Such structural models as GGG′G have not been taken up for other polymers because of the steric impact between the atoms in the helix. However, as we described in the previous paper, the –S–S– structures reduce the steric impact and make these structural models possible for polyalkyl polysulfides. The structural model for polymethylene disulfide was determined to be GG′G in the previous paper. This model is very similar to the present model for polyethylene disulfide. Apparently, therefore, such models as GG′G and GGG′G are characteristic of polyalkyl polysulfides.

For the models proposed by Katz and by Minoura, the internal rotation conformations have not been described explicitly. Therefore, we are able to derive the conformations only from the pictures in their papers.

For Katz's model, the internal rotation conformations appear to be trans, trans, trans and cis along the $-S-CH_2-CH_2-S-S-$ bond sequence of the 2_1 helical model. The skeletal atoms are placed on one common plane and twofold symmetry axes (intersecting the fiber axis at right angles) exist, in contradiction with the results of the present infrared analyses.

In Minoura's model, the internal rotation conformations appear to be gauche, trans, gauche and gauche, and the internal rotation angle around the S–S bond is implicitly assumed to be around 100°C. The helical model of the conformation is 2_1, and twofold symmetry axes (intersecting the helical axis at right angles) again exist. As we have proved in the present work, however, the twofold symmetry axes actually do not exist. Therefore, neither of their models can be accepted.

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