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Determination of the Crystal Structure of $(SN)_x$ by Neutron Diffraction

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The structure of the $(SN)_x$ polymer metal has been redetermined at room temperature by using neutron diffraction on single crystals. It is characterized by endless strands of N and S atoms with equal intrachain distances of $d\ (\text{S–N})_{\text{intra}} = 1.585$ Å. The intrachain bond angles at S and N atoms are 107.0 and 120.3°, respectively. The shortest interchain distances ($d(\text{S–N})_{\text{inter}} = 3.26$ Å, $d(\text{N–N})_{\text{inter}} = 3.34$ Å, and $d(\text{S–S})_{\text{inter}} = 3.47$ Å) are in the range of the sum of the van der Waals radii. Besides the N and S sites of the ordinary strands additional defect sites were found.

1. Introduction

In recent years $(SN)_x$ has attracted considerable interest because it is the first example of a polymer metal (*1*). Its electronic properties are highly anisotropic and therefore it was originally thought to be a new member of the class of quasi-one-dimensional conductors. However, recent results show that interchain coupling is much stronger in $(SN)_x$ than in typical quasi-one-dimensional metals, e.g., KCP or TTF–TCNQ.

Much theoretical effort has been spent on elucidating the band structure of $(SN)_x$, but for a long time that work suffered from a lack of reliable structural data. The first structural analysis of $(SN)_x$ was performed by a group in Lyon (Boudeulle *et al.* (*2*)) using electron diffraction. According to those authors $(SN)_x$ consists of endless strands of N and S atoms with alternating bond lengths corresponding to a single and a double bond, respectively. The interchain distances are much larger than these values, but some of them are considerably less than the sum of the van der Waals radii. Therefore, interchain coupling is expected to be rather strong.

Another structural determination was performed by a group at the University of Pennsylvania using X-ray diffraction (Cohen *et al.* (*3*)). Their results (in the following referred to as PENN structure) differ from the LYON structure in many important details:

(i) The intrachain bond lengths are found to be nearly equal.

(ii) The shortest interchain distances are barely less than the sum of the van der Waals radii, thus indicating a fairly weak interchain coupling.

(iii) There are additional, fractionally occupied sites, which implies a high degree of disorder on a molecular scale.

These discrepancies required further investigation. For this reason we started a neutron diffraction study.

2. Experimental

Single crystals of $(SN)_x$ were prepared by solid-state polymerization of vapor-grown

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S_2N_2 single crystals; details of the method of preparation have been published elsewhere (*4*). some 40 $(SN)_x$ crystals with volumes between 5 and 30 mm^3 were tested. The following results were obtained:

(i) The crystals are twinned on a microscopic scale via reflection in the (100) plane. The two twinning components are almost of the same size.[1]

(ii) Reflex scanning around the chain direction (*b*-axis) leads to huge linewidths (up to 11° f.w.h.m.), whereas the chain reflections (0*k*0) show normal linewidths. The $(SN)_x$ crystals consist of bundles of fibers (*1*). The strongly anisotropic mosaic spread means that the fibers are joined together with large angles of tolerance.

For the neutron diffraction study a single crystal of 15 mm^3 was chosen. Its mosaic spread in the (0*k*0) plane perpendicular to the chain direction and in the chain direction was found to be 9.5 and 2.1° (f.w.h.m.), respectively. The measurements were performed on the four-circle diffractometer P49 (λ_n = 0.9505 Å) at the FR2 reactor in Karlsruhe. For each of the two twinning components of the crystal 12 reflections were centered and the lattice parameters were determined by least-squares refinement. They were found to be equal within the limits of experimental error for both components (Table I). In this way we confirmed that our large samples consist of the usual β-modification of $(SN)_x$ only (*2*).

Because of the huge mosaic spread and its anisotropy with respect to the chain direction mentioned above, the usual method of data collection by ω-scans was not suitable in our case. This difficulty was overcome in the following way: We set our sample with its *b*-axis parallel to the φ-axis of the Eulerian cradle, and integral intensities of all (*hkl*) reflections except (0*k*0) were measured by φ-scans. The remaining (0*k*0) reflections were measured by conventional ω-scans. For the φ-scans the usual formula for the Lorentz correction has to be replaced by $1/L_\varphi = \sin 2\theta \cdot \cos\chi$.

For each twinning component a total of 153 symmetry-independent reflections (including 40 with $I < 3\sigma(I)$) were measured up to $\sin\theta/\lambda_n = 0.68$ Å^{-1}. According to the type of twinning the (*hk*0) reflections are common to both components. In detail there are 97 intensities observed separately for each twinning component and, in addition, another 16 for the common (*hk*0) reflections. Due to the intersection of the reciprocal lattices of the two twinning components, there are a few reflection profiles accidentally overlapping. In five cases we were not able to separate them. Those five reflections were rejected.

3. Refinement of the Structure

Reflex intensities calculated from the LYON structure showed serious deviations from the observed values. On the other hand, the parameters of the PENN structure were suitable for a least squares refinement. In our calculations we used the neutron scattering lengths: $b_N = 9.40 \times 10^{-15}$ m and $b_S = 2.847 \times 10^{-15}$ m (*5*). Using the space group $P2_1/c$ we refined the (*hkl*) intensities ($l \neq 0$) for each twinning component separately. With isotropic thermal parameters we arrived at values of the reliability factor $R_I = \Sigma|I_{\text{obs}} - I_{\text{calc}}|/\Sigma I_{\text{obs}} = 0.19$ and 0.23, respectively. The two resulting parameter sets were found to be in good mutual agreement. After this test the intensities of the two twinning components were summed up and completed by the common (*hk*0) reflection data. In this way an improved data set was constructed for the

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[1] Cohen *et al.* (*3*) report that they used an $(SN)_x$ crystal for their X-ray studies which showed only a very few reflections attributable to a twin. In the complete structure determination of the Moleculare Structure Corporation, available as supplementary material to their paper (*3*), a twinning of the used $(SN)_x$ crystal is not mentioned. However, a detailed comparison of the listed *F* values they observed and calculated shows systematic discrepancies for the (*hk*0) reflections. As these reflections are common to both twinning components, this is a strong indication of a certain amount of twinning that was not taken into consideration.

TABLE I

STRUCTURAL PARAMETERS OF $(SN)_x$

	LYON (*2*)	PENN (*3*) (Room temp.)	PENN (*3*) (−145 °C)	This study
Structure	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [Å]	4.12	4.153(6)	4.137(5)	4.11(1)
b [Å]	4.43	4.439(5)	4.431(4)	4.43(1)
c [Å]	7.64	7.637(12)	7.520(10)	7.63(1)
β[deg]	109.3	109.7(1)	109.53(9)	110.0(5)
S				
x	0.190	0.1790(8)	0.1813(7)	0.175(2)
y	0.106	0.7873(6)	0.7874(5)	0.789(2)
z	0.332	0.3443(4)	0.3449(4)	0.343(2)
o.p.[a]	1.0	1.0	1.0	0.90(1)
β_{11}[b]				0.050(6)
β_{22}				0.020(4)
β_{33}				0.018(3)
β_{13}				0.017(3)
N				
x	0.130	0.141(3)	0.143(3)	0.136(1)
y	0.454	0.431(2)	0.429(2)	0.432(1)
z	0.354	0.322(2)	0.325(1)	0.321(1)
o.p.[a]	1.0	1.0	1.0	0.90(1)
β_{11}[b]				0.071(2)
β_{22}				0.029(2)
β_{33}				0.015(2)
β_{13}				0.005(2)
Defect site 1, (S + N)/2				
x				0.27(1)
y				0.05(1)
z				0.37(1)
o.p.[a]				0.10(1)
β_{11}[b]				0.20(4)
β_{22}				0.07(3)
β_{33}				0.10(3)
β_{13}				0.13(3)
Defect site 2, (S + N)/2				
x				0.06(4)
y				0.76(1)
z				0.39(2)
o.p.[a]				0.10(1)
β_{11}[b]				0.87(28)
β_{22}				0.02(2)
β_{33}				0.29(9)
β_{13}				−0.50(17)

[a] o.p. = occupation probability.

[b] The atomic temperature factor T is defined as $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

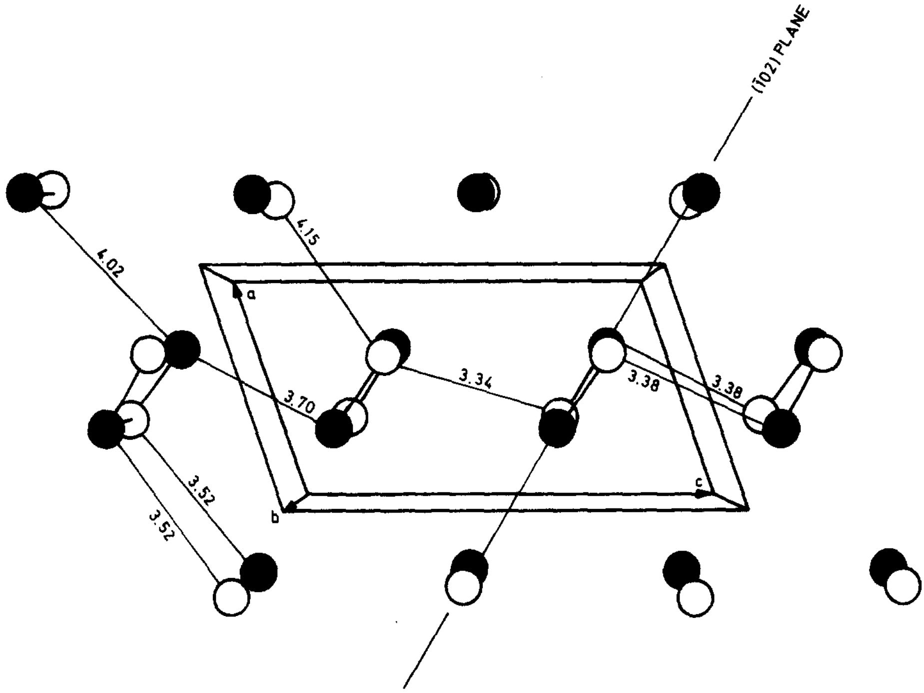

FIG. 1. The crystal structure of $(SN)_x$.

whole volume of the sample and calculations with anisotropic thermal parameters yielded an R_I-value of 0.109.

A subsequent difference Fourier analysis showed peaks at two symmetrically independent positions. We assumed a partial occupation of these sites by S and N atoms, respectively. A least-squares refinement of the atomic parameters as well as the occupation probabilities showed that the "main sites" are equally occupied by 90% forming the regular main chains. On the other hand the occupancies of the two additional positions differ by a factor larger than 3. These findings are inconsistent with the results of chemical analysis revealing an equal amount of sulfur and nitrogen in $(SN)_x$ crystals. Therefore we dropped our former assumption that each additional site is occupied either by N or S. On the assumption that equal amounts of sulfur and nitrogen are contained in the whole crystal the refinement yields a statistical occupancy of the defect sites half by N and half by S.

The final parameters are listed in Table I. Important distances and angles are given in Table II. The resulting R values are $R_I = 0.078$ and $R_F = \Sigma||F_{\mathrm{obs}}| - |F_{\mathrm{calc}}||/\Sigma|F_{\mathrm{obs}}| = 0.055$. In Table III there are listed the corresponding F_{obs} and F_{calc} values. Our findings are illustrated in Figs. 1–3.

4. Discussion and Conclusions

As can be seen from Table I, our results are in good agreement with the PENN structure, whereas there are major discrepancies relative to the LYON structure. Because of the close agreement between the X-ray and neutron diffraction results, and also because of the low R_I value of our refinement we believe the following structural statements to be reliable:

(1) The nearest-neighbor intrachain distances, within the limits of experimental error, are equal to $d(\mathrm{N{-}S})_{\mathrm{intra}} = 1.585$ (10) Å. According to the empirical relation between bond length and bond character n_{NS} $[d(\mathrm{N{-}S})]$

TABLE II

INTERATOMIC DISTANCES AND ANGLES

	LYON (*2*)	PENN (*3*)	This study
Distances [Å]			
Intrachain			
S–N	1.575 1.718	1.593 1.628	1.585(10)
	2.91	2.86	2.86(1)
N–N	2.72	2.58	2.55(1)
S–S	2.76	2.79	2.75(1)
Interchain (parallel ($\bar{1}02$))			
S–N	3.59	3.24	3.26(1)
N–N	3.15	3.33	3.35(1)
S–S	3.10	3.48	3.47(1)
Interchain (between ($\bar{1}02$) planes)			
S–N	3.60	3.37	3.38(1)
N–N	2.81	3.31	3.34(1)
S–S	3.55	3.72	3.70(1)
Angles [deg]			
Intrachain			
S–N–S	113.5	119.9	120.3(5)
N–S–N	111.5	106.2	107.0(5)

in N–S compounds given by Glemser *et al.* (*6*), the distance d(N–S) = 1.585 Å corresponds to $n_{NS} \approx 1.4$.

(2) The intrachain bond angles at S and N atoms are 107.0 (5) and 120.3(5)°, respectively.

(3) Each $(SN)_x$ chain is planar within experimental error. These planes are tilted against the ($\bar{1}02$) plane by an angle of 2.0(5)° around the [010] direction.

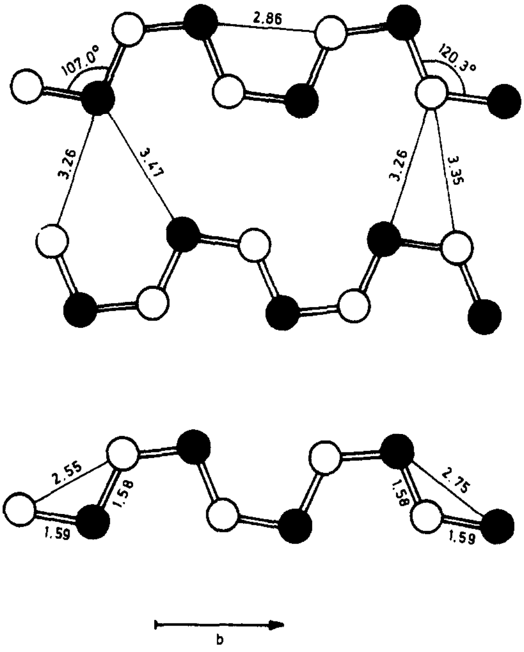

FIG. 2. Projection of $(SN)_x$ chains onto the ($\bar{1}02$) plane.

(4) The shortest interchain distances are found within the ($\bar{1}02$) plane: $d(S\text{–}N)_{inter}$ = 3.26(1) Å, $d(N\text{–}N)_{inter}$ = 3.35(1) Å, and $d(S\text{–}S)_{inter}$ = 3.47(1) Å. These values are considerably larger than those given by Boudeulle and in the range of the sum of the van der Waals radii.

(5) The interchain distances between neighboring planes are even larger than within the plane: $d(N\text{–}N)_{inter}$ = 3.34(a) Å, $d(S\text{–}N)_{inter}$ = 3.38(1) Å, and $d(S\text{–}S)_{inter}$ = 3.70(1) Å.

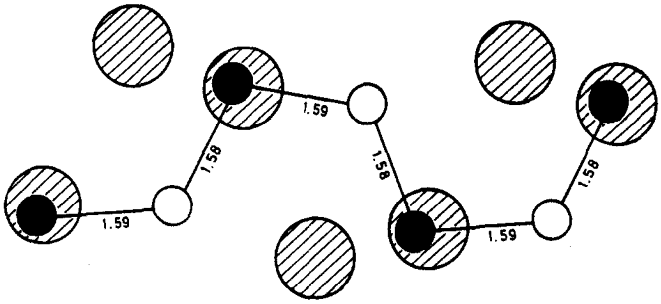

FIG. 3. Projection of an ordinary $(SN)_x$ chain and the defect S/N sites onto the ($\bar{1}02$) plane.

TABLE III

Observed and Calculated Structure Factors of $(SN)_x$[a].

h k l	F_{obs}	F_{calc}	h k l	F_{obs}	F_{calc}	h k l	F_{obs}	F_{calc}
0 1 6	15	16	−2 1 3	20	15	−1 4 1	33	37
−1 1 6	0	10	−3 1 3	37	36	−2 4 1	0	17
−2 1 6	0	2	−4 1 3	24	25	−3 4 1	0	5
0 0 6	66	69	0 5 2	24	25	3 3 1	0	5
−1 0 6	28	29	−1 5 2	0	0	2 3 1	16	19
−2 0 6	37	35	2 4 2	0	5	1 3 1	35	35
0 2 5	39	37	1 4 2	0	8	0 3 1	17	18
−1 2 5	0	7	0 4 2	0	1	−1 3 1	18	15
−2 2 5	40	40	−1 4 2	0	4	−2 3 1	31	31
1 1 5	0	6	−2 4 2	0	1	−3 3 1	14	16
0 1 5	47	49	−3 4 2	0	5	−4 3 1	0	4
−1 1 5	56	53	3 3 2	19	20	4 2 1	14	14
−2 1 5	25	21	2 3 2	25	26	3 2 1	40	41
−3 1 5	12	6	1 3 2	86	82	2 2 1	38	37
0 3 4	67	69	0 3 2	75	77	1 2 1	16	17
−1 3 4	64	63	−1 3 2	0	3	0 2 1	70	71
1 2 4	17	21	−2 3 2	58	58	−1 2 1	68	69
0 2 4	0	2	−3 3 2	50	51	−2 2 1	13	18
−1 2 4	19	21	−4 3 2	11	13	−3 2 1	28	27
−2 2 4	20	21	3 2 2	19	23	−4 2 1	25	28
1 1 4	20	20	2 2 2	18	16	4 1 1	12	15
0 1 4	15	16	1 2 2	0	6	3 1 1	10	9
−1 1 4	0	3	0 2 2	27	27	2 1 1	58	55
−2 1 4	0	2	−1 2 2	37	34	1 1 1	71	71
−3 1 4	0	3	−2 2 2	16	17	0 1 1	30	30
2 0 4	57	59	−3 2 2	0	4	−1 1 1	28	24
1 0 4	85	84	−4 2 2	0	1	−2 1 1	54	57
0 0 4	33	35	4 1 2	0	4	−3 1 1	41	42
−1 0 4	57	57	3 1 2	0	8	−4 1 1	0	7
−2 0 4	97	96	2 1 2	15	16	0 6 0	33	36
−3 0 4	47	44	1 1 2	12	10	−1 5 0	24	24
2 3 3	0	6	0 1 2	0	4	3 4 0	0	4
1 3 3	19	19	−1 1 2	0	1	2 4 0	0	5
0 3 3	32	33	−2 1 2	0	1	1 4 0	0	2
−1 3 3	23	18	−3 1 2	0	2	0 4 0	0	10
−2 3 3	0	10	−4 1 2	0	9	3 3 0	20	20
−3 3 3	18	23	4 0 2	0	4	1 3 0	74	74
−4 3 3	10	12	3 0 2	53	50	−2 3 0	70	69
3 2 3	14	20	2 0 2	84	84	4 2 0	13	15
2 2 3	49	49	1 0 2	37	38	3 2 0	12	10
1 2 3	44	41	0 0 2	71	73	2 2 0	0	4
0 2 3	11	13	−1 0 2	129	129	0 2 0	35	33
−1 2 3	56	59	−2 0 2	61	64	−1 2 0	24	23
−2 2 3	56	54	−3 0 2	20	21	4 1 0	10	9
−3 2 3	16	14	−4 0 2	38	43	3 1 0	18	15
−4 2 3	15	17	1 5 1	44	40	2 1 0	10	11
3 1 3	20	24	0 5 1	16	22	1 1 0	0	5
2 1 3	13	9	−1 5 1	15	18	4 0 0	34	36
1 1 3	59	58	2 4 1	11	12	3 0 0	66	65
0 1 3	69	69	1 4 1	16	18	2 0 0	28	29
−1 1 3	37	29	0 4 1	39	39	1 0 0	76	79

[a] F_{obs} values of 0 indicate the less than reflections ($I < 3\sigma(I)$); they were not used in the refinement.

(6) Besides the ordinary N and S sites there are additional defect sites. It seems obvious that the share of these disordered atoms strongly depends on the preparation of the crystals. In our case we found a ratio of 1 : 9 for defect and ordinary sites.

Defect sites have been predicted by Baughman *et al.* (7) on the grounds of a theoretical investigation of the solid-state polymerization of S_2N_2 to $(SN)_x$. Our defect positions are in qualitative agreement with these predictions. However, the following features are unexpected:

(i) The occupation of the defect sites is not unique, but each site is statistically occupied half by N and half by S.

(ii) The large "temperature factors" of the defect atoms indicate that their positions are not well defined. These differences do not exclude the concept of the defect atoms being arranged in disordered chain fragments.

Acknowledgments

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