

Structures of two crystal forms of poly(ethylene oxide)–sodium thiocyanate complex with molar ratios of 3:1 and 1:1

Yoza Chatani*, Yasuhiro Fujii, Tetsuya Takayanagi and Atsuya Honma

Department of Material Systems Engineering, Faculty of Technology,
Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan
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The poly(ethylene oxide) (PEO)–sodium thiocyanate system was found to exhibit polymorphism: there exist at least three crystal modifications. Among them, the crystal structures of two kinds of PEO–NaSCN complex with molar ratios (EO:NaSCN) of 3:1 (form I) and 1:1 (form II), respectively, were determined by X-ray diffraction. Crystal data are as follows: form I, monoclinic $P2_1/a$, $a=16.83$, $b=10.64$, c (chain axis) $=7.19$ Å†, $\gamma=125.5^\circ$ (c -unique), $N=12$ EO units (2 chains) and 4 NaSCN ions; form II, monoclinic $P2_1/c$, $a=7.55$, $b=12.10$, c (chain axis) $=5.83$ Å, $\beta=97.5^\circ$ (b -unique), $N=4$ EO units (2 chains) and 4 NaSCN ions. Form I has a crystal structure resembling that of the PEO–NaI complex. The polymer chains have a twofold helical structure of $(-t_2gt_2gt_2\bar{g}-)_2$ conformation, the chain repeat comprising six EO units. The helical polymer chain coils around an array of Na ions and each Na ion is coordinated by four polymer O atoms and two N of the SCN ions (the coordination number is six). In form II, which exists only under high tension, the polymer chains have a glide structure of $(-tg_2t\bar{g}_2-)$ conformation, the chain repeat comprising two EO units. Since the PEO chain in form II takes a rather stretched conformation, the Na ions are not wrapped by the polymer chain. The coordination number is again six, but each Na ion is coordinated by two polymer O atoms, two N and two S of the SCN ions. Form II is transformed into form I when the tension is released.

(Keywords: poly(ethylene oxide); sodium thiocyanate; poly(ethylene oxide)–sodium thiocyanate complex; polymorphism; crystal structure; X-ray diffraction)

INTRODUCTION

Much literature has appeared on complex formation of poly(ethylene oxide) (PEO) with organic and inorganic compounds in solutions or solids. In particular, crystalline or amorphous PEO complexes with alkali metal salts, first found by Wright¹, have been paid a great deal of attention as solid electrolytes or high ionic conductors^{2–4}.

In a previous paper⁵, the crystal structure of the PEO–NaI complex was revealed. The crystal structure is characterized by a NaI zigzag chain coiled round by a helical PEO chain having $(-t_2gt_2gt_2\bar{g}-)_2$ conformation, the chain repeat comprising six EO units. Hibma⁶ reported crystal data for the PEO–NaSCN complex, i.e. cell constants, space group and molar ratio (EO:NaSCN). In our laboratory, however, the PEO–NaSCN system was found to exhibit polymorphism. There exist at least three crystal modifications, named forms I, II and III. Form I is explained in terms of the Hibma cell. Form II, which exists only under high tension, has an unusually short chain repeat of 5.83 Å, differing from those of other alkali metal salt complexes (7–8 Å). In this paper, the crystal structures of PEO–NaSCN complex forms I and II will be reported.

EXPERIMENTAL

Samples

In contrast to the PEO–NaI complex, in the PEO–

NaSCN system X-ray photographs of various samples differed, indicating the existence of crystal modifications. Efforts were made to obtain samples containing only one crystal form.

Form I was obtained by casting PEO/NaSCN aqueous solutions or isopropylamine solutions with several molar ratios (EO:NaSCN) between 1:1 and 5:1. Differential scanning calorimetric (d.s.c) measurements together with X-ray measurements made by using the same technique as for the PEO–NaI complex⁵ suggested that the molar ratio of form I is 3:1 as reported by Hibma⁶. Stretching the cast film (3:1) gave oriented form I. More highly oriented form I was obtained by immersing a highly oriented PEO filament of ≈ 0.2 mm diameter into saturated NaSCN isopropylamine solution at room temperature without tension; completion of the conversion from PEO to form I was checked by disappearance of the X-ray diffraction pattern of PEO.

Further stretching the oriented cast film of form I and then holding it under high tension gave form II. Immersion of a highly oriented PEO filament into the NaSCN solution under high tension again gave form II. However, the samples obtained by the two techniques involved other crystal modifications. Note also that form II is converted into form I when the tension is released.

Form III was obtained when form I (3:1) was once melted and then stretched, if needed.

X-ray measurements

Nickel-filtered $\text{CuK}\alpha$ radiation was used throughout this study. Figures 1–3 show X-ray fibre photographs of

* To whom correspondence should be addressed
† $1 \text{ \AA} = 10^{-1} \text{ nm}$

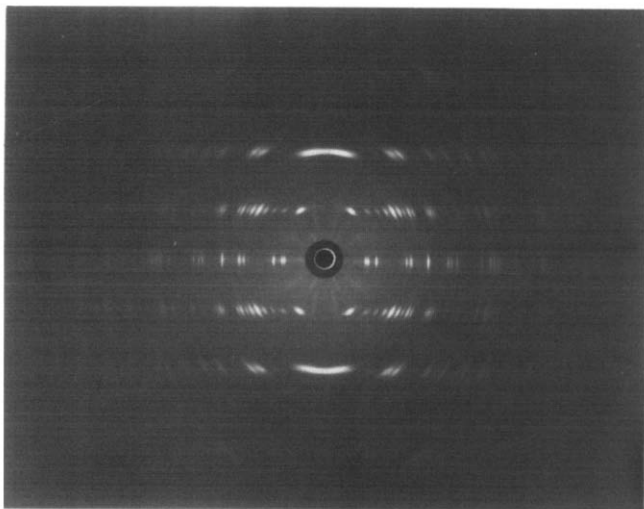


Figure 1 X-ray fibre photograph of PEO-NaSCN complex form I

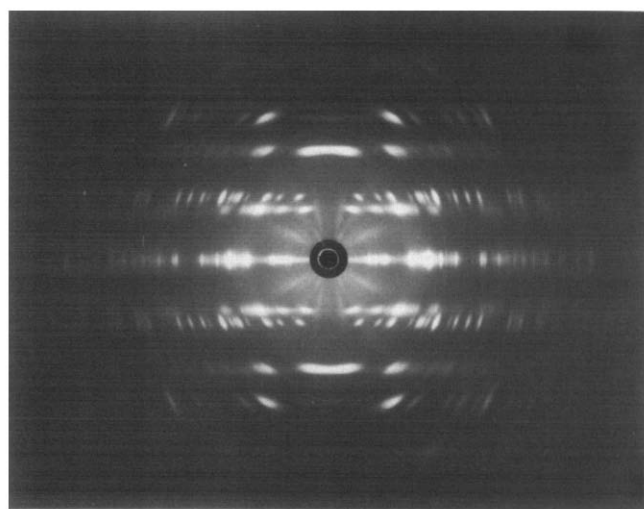


Figure 2 X-ray fibre photograph of PEO-NaSCN complex form II

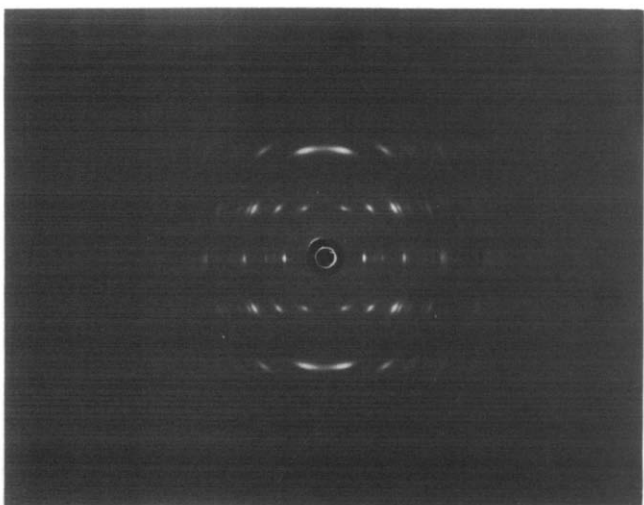


Figure 3 X-ray fibre photograph of PEO-NaSCN complex form III

forms I-III, respectively. The d -spacings of the reflections were measured with a cylindrical camera of 100 mm diameter and corrected with those of NaCl powder. The reflection intensities were obtained by the multiple-film method and measured visually with a standard intensity

scale. The observed intensities were corrected by the Lorentz polarization factor and the oblique effect for the layer lines.

Density measurements

The densities of the samples were determined by a flotation method using the densities of the liquid media (toluene + carbon tetrachloride) measured with a pycnometer.

STRUCTURE ANALYSIS

Form I

The X-ray fibre photograph of form I (Figure 1) is well explained in terms of the Hibma cell except for slight differences in cell constants. The crystal data are: monoclinic $P2_1/a$, $a = 16.83$, $b = 10.64$, c (chain axis) = 7.19 \AA , $\gamma = 125.5^\circ$ (c -unique), $N = 12$ EO units and 4 NaSCN ions (molar ratio = 3:1), observed density = 1.30 g cm^{-3} and calculated density = 1.35 g cm^{-3} . Form I has the same space group as the PEO-NaI complex. The molar ratio, 3:1, is also the same as that of the NaI complex. The crystal structure model was therefore obtained by trial and error with reference to the structure of the NaI complex, and the analysis was refined by the diagonal least squares method. The discrepancy factor, R , dropped to 11.6% for all the observed reflections ($R = \sum |I_o^{1/2} - I_c^{1/2}| / \sum I_o^{1/2}$, where $I = \sum mF^2$, m being the multiplicity of a reflection superimposed on one diffraction spot in the fibre photograph).

Form II

The X-ray fibre photograph of form II (Figure 2) involves diffraction patterns of other crystal forms, but form II gives layer lines at different levels from those of other crystal forms (forms I, II and III have chain repeats of 7.19, 5.83 and 7.13 \AA , respectively), and the equatorial reflections from form II could be readily distinguished from those of other crystal forms. The cell constants of form II were determined as $a = 7.55$, $b = 12.10$, c (chain axis) = 5.83 \AA and $\beta = 97.5^\circ$ (b -unique). The observed systematic absences of reflections ($h0l$ when l is odd, $0k0$ when k is odd and $00l$ when l is odd) indicate unequivocally that the space group is $P2_1/c$. In spite of the difficulty of density measurement on form II, the cell constants strongly suggest that there are four EO units and four NaSCN ions in the unit cell (the molar ratio is 1:1), and the number of general equivalent points for this space group, four, also supports this assumption, the calculated density being 1.57 g cm^{-3} . In addition, the observed chain repeat, 5.83 \AA , is very close to that of the PEO-HgCl₂ complex form II (5.88 \AA), in which the PEO chains take a glide structure of $(-tg_2tg_2-)$ conformation⁷, the chain repeat comprising two EO units. The space group $P2_1/c$ enables PEO to make the chain repeat by two equivalent EO units related by the c -glide plane. Based on these assumptions, a reasonable structure model was obtained by trial and error. The structure was refined by the diagonal least squares method. The R factor dropped to 10.0% for all the observed reflections.

Fractional atomic coordinates and thermal parameters for forms I and II are listed in Tables 1 and 2, respectively. Observed and calculated structure factors for forms I and II are listed in Tables 3 and 4, respectively.

Table 1 Fractional atomic coordinates and thermal parameters for form I

	x	y	z	B (Å ²)
Na	0.226	0.957	0.917	5.5
S	0.219	0.362	0.651	5.4
C	0.224	0.224	0.662	5.4
N	0.226	0.102	0.655	6.0
O1	0.062	0.863	0.022	5.5
C1	0.057	0.922	0.200	5.5
C2	0.124	0.091	0.210	6.0
O2	0.220	0.141	0.158	5.9
C3	0.277	0.297	0.151	4.5
C4	0.377	0.346	0.127	5.7
O3	0.393	0.295	0.294	5.4
C5	0.489	0.348	0.324	5.0
C6	0.496	0.294	0.518	5.8

Table 2 Fractional atomic coordinates and thermal parameters for form II

	x	y	z	B (Å ²)
Na	0.539	0.339	0.382	4.1
S	0.258	0.461	0.594	4.0
C	0.346	0.393	0.819	4.0
N	0.411	0.331	0.986	4.2
O	0.770	0.252	0.692	4.2
C1	0.807	0.336	0.859	4.2
C2	0.909	0.283	0.072	4.1

Table 3 Observed (F_o) and calculated (F_c) structure factors for form I

hkl	F_o	F_c
010	61	56
-210	58	61
200	90	98
210, 020	54	46
-410, -420	79	75
400, -430, -230	112	99
220	21	26
030	67	69
-620	61	64
410, -630	69	82
-240	19	13
600	62	64
420, 040	69	60
-830, -450	61	62
-650	41	42
-820, -840	44	36
-250	22	23
610	38	53
-810	34	37
-850	39	39
240	27	29
800, 050, -460	38	47
-(10)40, -860	32	25
620, -(10)30	59	55
-(10)50, -260	27	42
810, -670	16	17
-(10)10, -870	34	22
440, 250	16	14
-(12)40, -(10)70	34	39
(10)00, -(12)30, -270	25	13
-880, -680	29	29
-(12)70, -(10)80	24	33
450, 260, -480	23	26
(10)10, 640	26	25
-(12)10	21	14
830, -(14)50	20	25
-280, -890	21	21
-(14)30, -690	20	17
(12)00, (10)20	21	21
650, -490, 270	30	26

Table 3 (Continued)

hkl	F_o	F_c
840	18	5
(12)10, (-16)60, -(14)90, -8(10)0, -(16)50, -(12)(10)0, -(16)70, -(14)10	16	18
101	65	57
011	28	23
-211	22	19
201	37	39
111	53	57
-311	19	29
-221	113	109
-321	78	68
301	52	49
211, 021	77	72
-411, -421	62	56
121, -331	57	50
401, -231	70	69
311, -521, -431	45	44
-511, -131	39	47
-531	28	28
221	31	21
411, -631	52	53
321, 131, -241	28	23
-721, -731, -141	55	51
511, 231, -741	57	54
-711	48	44
421, 041	33	33
-831, -451	33	26
-821, -841	24	30
331, 141, -251	30	28
-811	25	28
521, -931, -941, -151	50	43
431, -951, -661, -561	21	22
801, 711	53	49
-911, -(10)31, -(10)41, -861, -361	56	62
341, 151, -961, -261	39	40
531	19	22
901, 811, -(11)31, -(11)51, -771, -671	39	45
721, 441, 251, -871, -571	22	34
-971, -471	32	35
-(11)21, 631, -(11)61, 061	21	21
-(11)11, 821, 541, -(12)61, 161, -(11)71, -271	34	38
-(12)21, 731, -171, -981, -581	25	25
(11)01, (10)11, -(13)31, 641, 071	24	22
-(13)21, 831, -(14)61, 361	25	29
-112, 012	35	39
202	30	31
-312	61	65
-222, -122	75	77
-322	83	85
302	38	46
-412, -422	31	30
402, 122, -332, -232	63	71
312, -522, -432	30	37
-512, -132	41	47
-532	63	62
-622	28	20
502, 412, -632	34	33
-612, -442, -342	61	66
-542	29	32
-722, -142, -732	63	64
512, 232, -742	39	39
-712	34	42
-832, -652, -552, -452	37	38
-822, -842	27	25
702, 612, 332, 142, -252, -752	47	47
-932, -852, -152	37	41
432, -952, -662, -562, 242	41	39
052, -762, -462	29	25
802, 712, -862, -362, -(10)42	33	22
-912, 622, -(10)32	25	37
-(10)22, 152, -962, -262	33	26
532	23	17
902, 812, -(11)42, -(10)62, -162, -772, -672	33	27
-(11)22, -(11)62, 062	28	24

Table 3 (Continued)

<i>hkl</i>	F_o	F_c
912, -(12)32, 542, 352, -(12)62, 162, -(11)72, -272, -(11)12, (10)02	37	31
732, -(13)42, -(13)52, -(12)72, -172, -(10)82, -582, -(12)22	30	29
-313, 113	18	20
-323, -223, -123	37	41
303, 213, 023	29	29
-413, -423	25	23
123, -333, -233	54	54
403, 313, -523, -433	47	54
-533	36	47
223, 033	27	29
503, 413, -633	38	36
-613, -543, -443, -343	29	34
323, 133, -243	24	25
603, 513, 233, -743, -713	41	36
423, -833, -553, -453	36	31
-843, -823, -353, -653	25	19
703, 613, 333, 143, -253	32	32
-813, 523, -933, -853, -153, -943	35	31
433, -953, -763, -663, -563, -463, 243	26	24
803, 713, 053	28	25
-913, 623, -(10)33, -(10)43, -863, -363	32	33
903, 813, -(11)33, -(11)43, -(11)53, -163, -773, -673, -573	39	43

Table 4 Observed (F_o) and calculated (F_c) structure factors for form II

<i>hkl</i>	F_o	F_c
100	42	40
110	48	44
020	37	38
200	47	43
210, 130	114	119
220	66	56
140	60	55
300	17	18
240	58	60
320, 150	47	47
330	43	40
250, 060	25	25
160	36	42
400	35	36
410	27	28
420, 260	39	41
350	21	23
430, 170	38	41
440	30	28
360, 270	25	24
510, 450	26	26
370	40	38
530, 280	22	22
190	17	7
550, 470	25	27
600, 610	18	22
0(10)0	24	25
390	15	12
640, 2(10)0	26	27
570	19	23
650	19	19
490, 3(10)0, 1(11)0	20	25
700, 710	14	11
2(11)0, 720	13	11
670, 4(10)0	16	23
590, 3(11)0, 1(12)0	17	16
750, 2(12)0	20	15
800, 810, 5(10)0, 3(12)0, 820	19	21
011	29	27
-111	30	27
021	23	21
111	44	41
121	28	22

Table 4 (Continued)

<i>hkl</i>	F_o	F_c
031	49	48
-211	45	48
-131	36	33
-221, 131	82	80
221, 041	33	36
-231, -141	53	47
141	11	10
-311, 231	56	55
-321, -241, 051	60	60
311, -151	15	11
241, 151	19	26
321, -331	23	26
331	47	43
-341, 251, -161	31	36
061	8	9
-411, 161	46	44
-421, 341	21	22
-261	10	11
411, -431, -351	28	27
421, 261, 071	22	16
431, -441	23	24
-511, 441, 271	21	20
361, -451, 081	16	17
-181, 181	27	26
511, -531, 451, -371	21	26
521, -281	14	22
-541, 281	30	34
461, 091	28	25
541, -551, -381, 191	31	32
-611, 381, -291	29	31
551, 471, 291	13	13
-481, -391, -1(10)1, 0(10)1, 611	20	20
-641, 561, 1(10)1	13	12
631, 391	14	19
641	10	13
571, -491, 0(11)1	13	14
-721, -581, 491, 3(10)1, 1(11)1, -661	15	16
711, 581, 2(11)1	14	14
721, -741, -671, -4(10)1	13	13
-751, 4(10)1, -1(12)1, 0(12)1, -3(11)1	10	8
741, 591, 1(12)1	18	18
-811, 751, -761, -4(11)1, -5(10)1	16	18
761, -771, -691, 5(10)1, 3(12)1, -1(13)1, 0(13)1, -831	18	17
-112	16	17
102, 022	29	29
112, -122	64	68
-212, 122, 032	40	40
-222	22	22
202, 132	14	17
212	33	32
-302, 222	40	38
-312	23	25
-322, 232, -242	35	36
052, -152	72	75
302, 152	12	13
242, 312	16	10
322, -252	27	32
-402, -342	18	17
-412, 062	24	25
-422, 252	30	35
162	29	33
-432, -352, -262	13	13
342	21	19
402, 412, 072, -172	16	15
422, 352, -362, 172	36	36
-502, -512, -272	22	23
-522, -452	28	30
272, 082	32	31
-372, 182	19	22
-462, -282, -542	17	18
502, 512, 452	27	31
522, 372, 282	18	22
532, -552, -382, -192, 092	18	19
-612, 462, -472, -602, 192	26	30
362, -562	13	17

Table 4 (Continued)

hkl	F _o	F _c
292	16	15
-642, 552, -482, -392, 0(10)2, -1(10)2, 472	19	16
602, 612, -572, 1(10)2, -2(10)2	21	19
-702, -712, 632, 482, 2(10)2, -492	16	16
-722, 642, -662, -582, -3(10)2, 0(11)2, -1(11)2	25	23
-223, 123, -133, 033	17	22
-233, 133	39	43
-313, 213, -143, 043	34	33
-323, 223	31	30
-333, 233, -153, 053	47	48
-413, 313, -343, 243, -253, 153	28	22
323, -163, 063	21	21
333, -353, 253, -263, 163	32	35
-443, 343, 073, -173	22	20
413, -523, -273, 173, -513	33	31
-373, 273, -183, 083	26	23
443, -283, 183, -543, 363, -463	36	29
-623, 523, -473, 373, -383, 283, -193, 093, 513, -613	33	31
-633, 533, -563, 463, -293, 193	23	19
543, -483, 383, -643	25	24
-573, -1(10)3, 0(10)3, 473, 553, -653, 473	16	13

RESULTS AND DISCUSSION

Form I

The molar ratio (EO:NaSCN) of form I is 3:1. The crystal structure of form I is shown in Figure 4. The structure is analogous to that of the PEO-NaI complex. The PEO chains have a twofold helical structure of $(-t_2gt_2gt_2\bar{g}-)_2$ conformation, where C-O bonds are *trans* (*t*) and C-C bonds are *gauche* (*g*) or *-gauche* (\bar{g}), and the chain repeat comprises six EO units. Bond lengths, bond angles and internal rotation angles are shown in Table 5. The SCN ions, which bend about 4°, are stacked horizontally along the chain axis. In Figure 4, the coordination geometry about a Na ion is shown by broken lines. Along the chain axis, Na and N are coordinated alternately. Each Na ion is coordinated by four polymer O atoms. The coordination number is therefore six. The coordination distances are listed in Table 6 (reported distances are 2.22–2.75 Å for Na···O⁸, 2.826 Å for Na···S⁸, and 2.332 Å for Na···N⁹). Since all the Na···S distances in form I are >4.17 Å, there is no coordination between Na···S.

In spite of the similarity between the crystal structures of the PEO-NaI complex and of form I, the coordination number in the NaI complex is not six, but five (two I ions and three O atoms). Na···I distances in the NaI complex are 2.92 and 3.20 Å alternately (for comparison, Na···N distances in form I are 2.15 and 2.44 Å alternately). The chain repeat in the NaI complex (7.98 Å) is then 0.79 Å longer than that of form I in order to achieve both Na···I and Na···O coordinations. These features appear to bring about the difference in coordination number.

Form II

The molar ratio of form II was determined by the present X-ray study as 1:1. The crystal structure of form II is shown in Figure 5. The PEO chains have a glide structure of

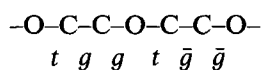


Table 5 Bond lengths, bond angles and internal rotation angles in form I

Bond length (Å)	
O1-C1	1.45
C1-C2	1.57
C2-O2	1.47
O2-C3	1.44
C3-C4	1.51
C4-O3	1.40
O3-C5	1.43
C5-C6	1.53
C6-O1'	1.45
S-C	1.51
C-N	1.31
Bond angle (deg)	
C6'-O1-C1	112
O1-C1-C2	112
C1-C2-O2	115
C2-O2-C3	113
O2-C3-C4	113
C3-C4-O3	100
C4-O3-C5	112
O3-C5-C6	106
C5-C6-O1'	109
S-C-N	176
Internal rotation angle (deg)	
C6'-O1-C1-C2	177
O1-C1-C2-O2	-52
C1-C2-O2-C3	174
C2-O2-C3-C4	171
O2-C3-C4-O3	-64
C3-C4-O3-C5	-170
C4-O3-C5-C6	175
O3-C5-C6-O1'	56
C5-C6-O1'-C1'	178

Table 6 Coordination distances in form I

Coordination distance (Å)	
Na···O (1) ^a	2.52
Na···O (2)	2.58
Na···O (3)	2.53
Na···O (4)	2.65
Na···N (5)	2.41
Na···N (6)	2.15

^a Numbers in brackets are explained in Figure 4

Table 7 Bond lengths, bond angles and internal rotation angles in form II

Bond length (Å)	
O-C1	1.40
C1-C2	1.52
C2-O'	1.41
S-C	1.61
C-N	1.28
Bond angle (deg)	
O-C1-C2	107
C1-C2-O'	102
C2'-O-C1	118
S-C-N	174
Internal rotation angle (deg)	
C2'-O-C1-C2	-77
O-C1-C2-O'	-88
C1-C2-O'-C1'	159

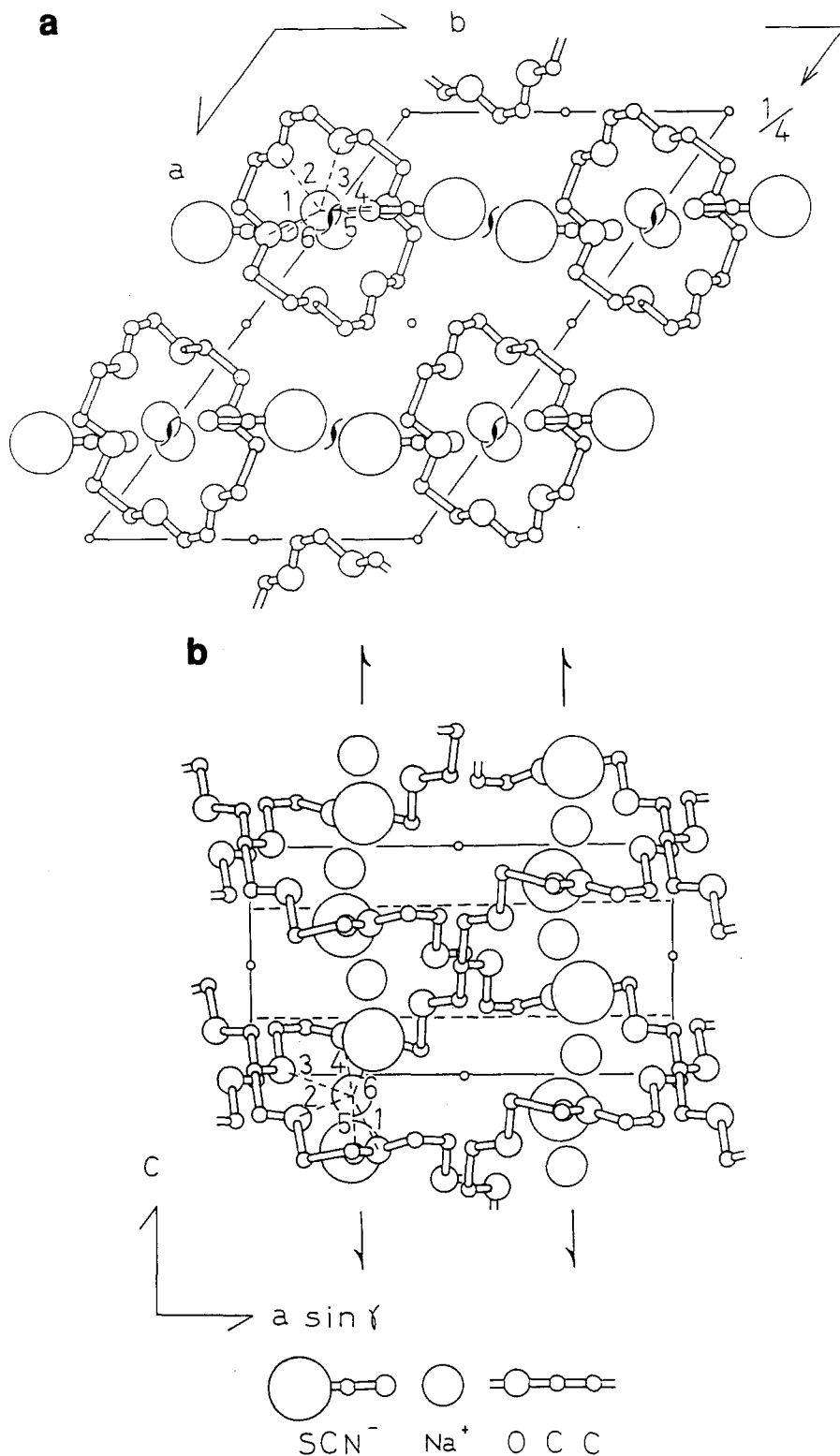


Figure 4 Crystal structure of PEO-NaSCN complex form I: (a) *c* projection and (b) $-b$ projection

conformation, the chain repeat comprising two EO units. Bond lengths, bond angles and internal rotation angles in form II are listed in Table 7. The coordination number in form II is again six. However, differing from form I, in which the SCN ion is coordinated to Na via the N atom, the S of the SCN ion also participates in coordination in form II, as shown by broken lines in Figure 5. Each Na ion is coordinated by two polymer O atoms and two N and two S of the SCN ions. The coordination distances are listed in Table 8.

Table 8 Coordination distances in form II

Coordination distance (Å)	
Na...O (1) ^a	2.58
Na...O (2)	2.44
Na...N (3)	2.37
Na...N (4)	2.39
Na...S (5)	2.98
Na...S (6)	2.86

^a Numbers in brackets are explained in Figure 5

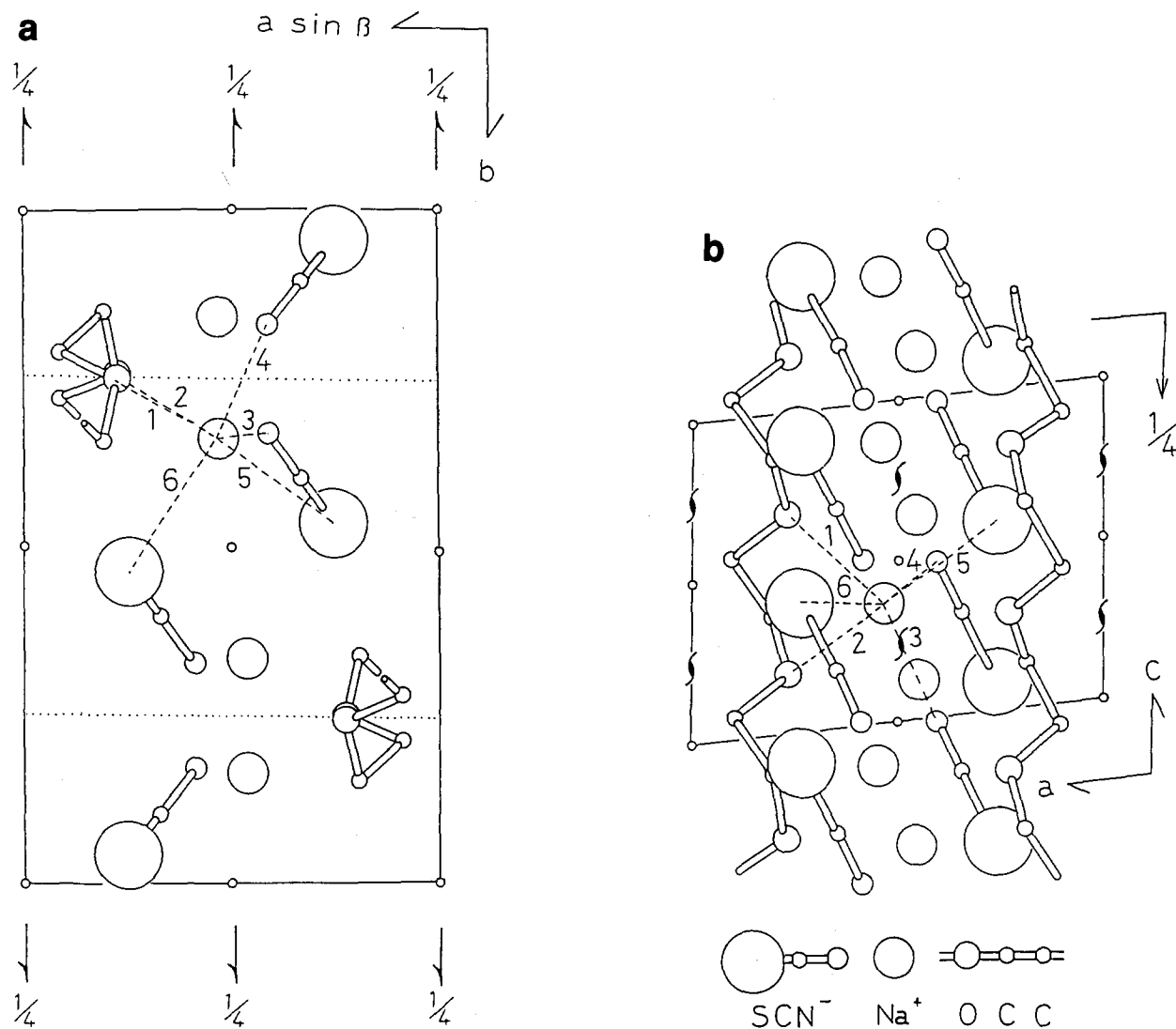


Figure 5 Crystal structure of PEO-NaSCN complex form II: (a) c projection and (b) b projection

In the PEO-NaI complex and form I, the helical polymer chain coils round the cations, but this is not the case in form II. The interval of EO units along the chain axis in form II ($5.83/2 = 2.92 \text{ \AA}$) is considerably longer than the average interval in form I ($7.19/6 = 1.20 \text{ \AA}$). Accordingly, the rather extended PEO chain in form II is unable to wrap Na ions. Since the $(-tg_2tg_2-)$ conformation itself must be energetically unstable, it is readily understandable that form II exists only under high tension (for comparison, for PEO, the fully extended zigzag form¹⁰ exists only under high tension). In practice, form II is transformed into form I when the tension is released. On this transformation, the molar ratio of 1:1 in form II changes to 3:1 in form I. However, no appreciable free NaSCN crystals were detected by X-rays after completion of the transformation. Probably the excess NaSCN dissolves in amorphous parts or is spent to develop form I crystallites with PEO in amorphous parts. Although the structure of form III is not known,

dependence of the electric conductivity on polymorphism may be of interest.

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