

Structural Studies of Polyesters. IV. Molecular and Crystal Structures of Poly(ethylene succinate) and Poly(ethylene oxalate)

Akio S. UEDA,* YOZO CHATANI, and HIROYUKI TADOKORO

Department of Polymer Science, Faculty of Science, Osaka University
Toyonaka, Osaka, Japan, 560.

(Received December 21, 1970)

ABSTRACT: In the course of structural studies of aliphatic polyesters of the type $[-O-(CH_2)_x-O-CO-(CH_2)_y-CO-]_n$, the molecular and crystal structures of poly(ethylene succinate) ($x=2, y=2$) and poly(ethylene oxalate) ($x=2, y=0$) were determined by interpretation of X-ray diffraction patterns and complementary study of infrared spectra.

The crystallographic data are:

Poly(ethylene succinate); $a=7.60 \text{ \AA}$, $b=10.75 \text{ \AA}$, c (fiber axis) $=8.33 \text{ \AA}$, orthorhombic space group $Pbn\bar{2}_1$, four molecular chains pass through the unit cell.

Poly(ethylene oxalate); $a=6.44 \text{ \AA}$, $b=6.22 \text{ \AA}$, c (fiber axis) $=11.93 \text{ \AA}$, orthorhombic space group $Pbcn$, two molecular chains pass through the unit cell.

The chain conformation of poly(ethylene succinate) is $T_3GT_3\bar{G}$, in which the two $C(H_2)-C(H_2)$ bonds in the chemical repeating unit are G or \bar{G} , where T means *trans* form and G and \bar{G} are used to discriminate right-handed and left-handed *gauche* forms, respectively. The chain conformation of poly(ethylene oxalate) is $T_3GT_3\bar{G}$, in which the $C(H_2)-C(H_2)$ bond is G or \bar{G} . There are some close similarities between the molecular and crystal structures of poly(ethylene succinate) and poly(ethylene oxalate), and their structures are quite different from polyethylene-like structures for the higher members ($x=2, y \geq 4$) of the ethylene glycol series. The high melting points of poly(ethylene succinate) and poly(ethylene oxalate) among the homologous polymers may be related to these molecular and crystal structures.

KEY WORDS X-ray Diffraction / Infrared Spectra / Crystal Structure / Poly(ethylene succinate) / Poly(ethylene oxalate) / Conformation /

Crystal structures of various kinds of aliphatic polyesters of the type $[-O-(CH_2)_x-O-CO-(CH_2)_y-CO-]_n$ were first studied by Fuller and his collaborators.¹⁻⁴ As for polyesters of the ethylene glycol series ($x=2$), they found that the observed lengths of chemical repeating units of the numbers of y higher than 4 were slightly shortened (about 0.5 \AA) from the calculated lengths of the fully extended zigzag forms, and the even members of y were crystallized in monoclinic forms while the odd members of y were in orthorhombic forms, though the lateral arrangements of the chains in these members were quite similar to that found in polyethylene.⁵

* Present address: The Central Research Laboratories, Chisso Corporation, Kamariya, Kanazawa-ku, Yokohama, Japan.

It is already known, however, that in poly(ethylene succinate) ($y=2$), the fiber period is shortened about 1.47 \AA from the fully extended form. Fuller, *et al.*,¹ proposed a molecular model taking the chain conformation of $(TGT\bar{G})_2$, in which the $C(H_2)-C(H_2)$ bonds in the glycol and acid parts are right-handed *gauche* form (G) or left-handed *gauche* form (\bar{G}) and the other bonds are *trans* form (T). They also proposed a monoclinic unit cell having the cell dimensions of $a=9.05 \text{ \AA}$, $b=11.09 \text{ \AA}$, c (fiber axis) $=8.32 \text{ \AA}$ and $\beta=102.8^\circ$. But they did not carry out further investigation on this subject. Later Bunn⁶ suggested that the chain conformation of $(TG)_2(T\bar{G})_2$ (or $(AB)_2(AC)_2$ in Bunn's designation) is also eligible from consideration of the fiber period and nonbonded atomic dis-

tances. In spite of being paid such attentions, the molecular conformation and crystal structure of poly(ethylene succinate) remained to be determined.

As for (polyethylene oxalate) ($y=0$), no X-ray investigations have been reported. But this simplest polyester of the ethylene glycol series shows some peculiar characteristics⁷ and the highest melting point (172°C) among the homologous polyesters.

It is important, therefore, to determine the molecular and crystal structure of these polyesters which could conceivably have non-polyethylene-like structures.

STRUCTURE DETERMINATION

Materials

Samples of poly(ethylene succinate) (PES) and poly(ethylene oxalate) (PEO) were prepared from ethylene glycol with succinic acid and oxalic acid, respectively. PES thus obtained was highly crystalline, but could hardly be drawn due to its low molecular weight. Therefore the polymer was treated with toluylene diisocyanate to produce a higher molecular weight compound. Such a procedure was similar to the case of polyethylene adipate reported by Turner-Jones and Bunn.⁸ Uniaxially oriented samples of PES for the present X-ray study were obtained by quick quenching of the molten sample in Dry Ice—methanol followed by cold drawing. On the other hand, PEO was stretched at 70°C under normal atmospheric conditions and annealed for several hours to crystallize at 100°C. In the annealing process, PEO filaments became elongated and highly oriented samples were hardly obtained at all.

Unit Cell and Space Group

Throughout the present X-ray study nickel-filtered $\text{CuK}\alpha$ radiation (wave length 1.542 Å) was used. From X-ray fiber photographs, shown in Figures 1 and 2, the cell dimensions of the orthorhombic system for PES and PEO were determined. The cell dimensions thus obtained were as follows

PES; $a=7.60$ Å, $b=10.75$ Å, $c(\text{fiber axis})=8.33$ Å,
PEO; $a=6.44$ Å, $b=6.22$ Å, $c(\text{fiber axis})=11.93$ Å.
The number of chemical repeating units per unit cell is four for PES and PEO. The observed

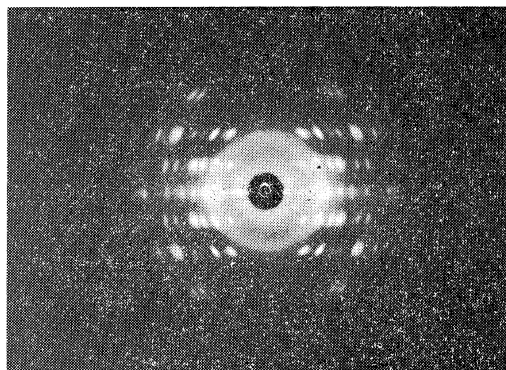


Figure 1. X-ray fiber photograph of poly(ethylene succinate).

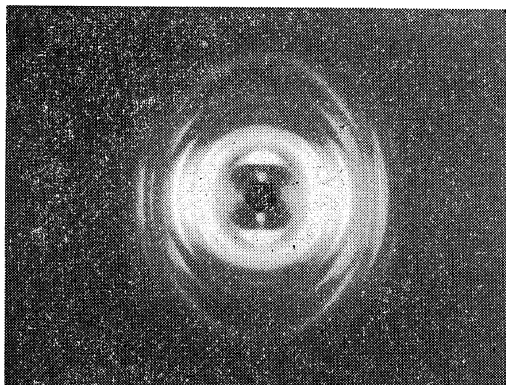


Figure 2. X-ray fiber photograph of poly(ethylene oxalate).

and calculated densities are 1.35 g/cm³ and 1.41 g/cm³ for PES, and 1.57 g/cm³ and 1.61 g/cm³ for PEO, respectively. The observed spacings in PES by Fuller and the present authors are in accord with each other within experimental accuracy. However, all observed reflections were satisfactorily indexed by the present orthorhombic cell rather than the monoclinic cell of Fuller, *et al.* The systematic absences of the X-ray reflections are: $hk0$ absent when k is odd, $h0l$ when $h+l$ is odd and $0k0$ when k is odd for PES, and $0kl$ absent when k is odd, $h0l$ when l is odd and $hk0$ when $h+k$ is odd for PEO. Therefore the space groups are determined as Pbnb-D_{2h}^{10} for PES and Pbcn-D_{2h}^{14} for PEO.

Intensity Measurement

Reflection intensities of the fiber diagrams were recorded by using a cylindrical camera.

In these photographs, the multiple film method was used. The intensities of the reflection spots were measured for visual comparison with an intensity scale and corrected for the oblique effect. The usual Lorentz-polarization factor and multiplicities of reflections were applied to obtain observed structure factors. In order to record the $(00l)$ reflections and the layer lines higher than the 5-th layer line of PES, a Weissenberg photograph was taken with the direction perpendicular to the fiber axis as the rotation axis. In addition to these photographs, a single crystal diffractometer from Rigaku Denki Co. Ltd. was used for the fiber sample. Though only comparatively strong reflections could be detected by the diffractometer, these data were available to adjust scaling factors for each layer line. As already mentioned, well oriented samples of PEO were not obtained. The intensity measurement for PEO, therefore, was made using a powder sample with photographs and a diffractometer. The fibre photograph was used to separate individual reflection intensities, since intensities of individual reflections were necessary—at least qualitatively—in the course of structure refinement.

Molecular Conformation and Crystal Structure Determination

PES. From the observed fiber period of 8.33\AA , we found that there are three kinds of possible skeletal conformations of PES, *i.e.*, in addition to $(\text{TGT}\bar{\text{G}})_2$ proposed by Fuller and $(\text{TG})_2(\text{T}\bar{\text{G}})_2$ by Bunn, $\text{T}_3\text{GT}_3\bar{\text{G}}$ is also possible. Moreover it is possible to construct many different models from each of the skeletal conformations mentioned above, depending on which skeletal bond takes the *trans* or *gauche* form. On the other hand, from the requirement of the Pbnb space group, since there are eight general equivalent positions in this space group, and four molecular chains pass through the unit cell, the molecule must have either twofold rotation axes perpendicular to the fiber axis or centers of symmetry (Figure 3). Only two cases are permitted; one is that the molecule itself has centers of symmetry and these centers of symmetry fit the centers of symmetry of the unit cell, and the other is that the molecule has twofold rotation axes perpendicular to the fiber axis and these axes coincide with those of the unit cell, parallel to the b axis. Based on these restrictions, six molecular models shown in Figure 4 can be proposed. Here the symbols C_2 and i are used to discriminate the models having twofold axes

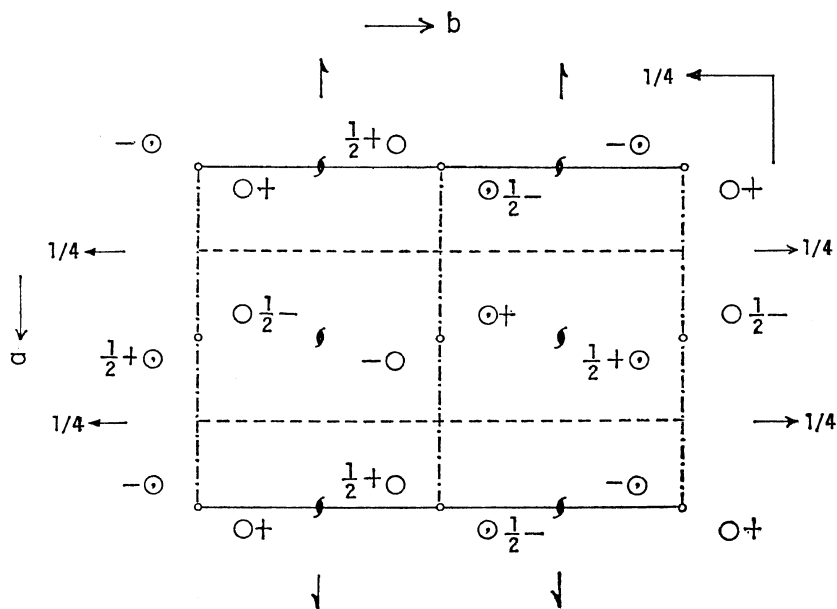


Figure 3. Equivalent positions in the space group Pbnb-D_{2h}^{10} for poly(ethylene succinate).

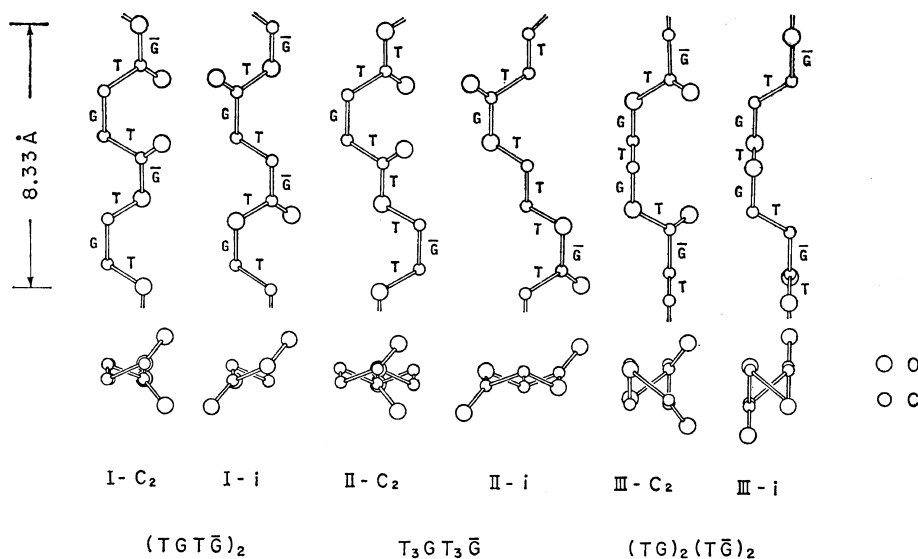


Figure 4. Possible conformations of poly(ethylene succinate). The true one is II-C₂ as shown in text.

and center of symmetry, respectively. In these models, I-C₂ is the Fuller's model and III-i is Bunn's model.

At first whole models having centers of symmetry, I-i, II-i, and III-i, were excluded, by comparison of observed and calculated structure factors of the equatorial (*hk0*) reflections. These models must locate in such a manner that the centers of symmetry of the molecules fit the centers of symmetry of the unit cell. Therefore, the positional freedom of molecules is restricted only within rotation around the *c* axis. No close agreement of observed and calculated structure factors in (*hk0*) reflections could be obtained in any orientation for the three models having centers of symmetry. Factor group analysis of infrared spectra also ruled out these three models. Next, in order to select a reasonable conformation from the three models having twofold rotation axes, structure factors of (*00l*) reflections were evaluated. I-C₂ and II-C₂ models gave the same calculated values and they agreed well with those observed. But III-C₂ did not agree; the observed intensity of (004) reflection was about ten times that of (002), while the calculated intensities of the two reflections were almost the same. III-C₂ was thus excluded at this stage.

Normal coordinate treatments for the skeletal

vibrations of these three models having twofold rotation axes were also attempted using force constants⁹ for the planar zigzag polylactone series. Model III-C₂ was excluded for poor agreement between the observed and calculated frequencies. Since force constants had not been adequately refined at this stage of the calculations, it was not possible to reliably determine which model was reasonable, I-C₂ or II-C₂. But the average errors for I-C₂ and II-C₂ were 7 and 5% at that stage, respectively, and it suggested the possibility of II-C₂ in addition to I-C₂.¹⁰

It was rather difficult to determine the true

Table I. Atomic coordinates and thermal parameters of poly(ethylene succinate)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
C(4) ^a	0.719	-0.013	0.663	5.0
C(3)	0.787	0.094	0.571	5.0
C(2)	0.798	0.198	0.331	5.0
O(2)	0.724	0.099	0.422	5.0
O(3)	0.903	0.161	0.615	7.5
H(1)	0.760	-0.097	0.600	7.5
H(2)	0.575	-0.013	0.665	7.5
H(3)	0.939	0.190	0.316	7.5
H(4)	0.765	0.282	0.396	7.5

^a As to the numbers in parentheses, see Figures 6 and 9.

Poly(ethylene succinate) and Poly(ethylene oxalate)

molecular structure of the remaining two models, I-C₂ or II-C₂. In the lattice of space group D_{2h}¹⁰-Pbnb the model having C₂ symmetry has only a translational freedom along the glide plane parallel to the *b* axis, since the twofold rotation axes of the model must fit the twofold rotation axes parallel to the *b* axis of the lattice (Figure 3). Moving the models along the *b* axis in the range between *y*=0 and 1/2, calculated

structure factors of (*hkl*) reflections were compared with the observed ones. The II-C₂ model was then found to be true one. Hereafter the atomic coordinates were refined successively by trial and error procedures. In the final stage the contribution of the hydrogen atoms was included in the structure factor calculation, assuming the C-H bond length of 1.09 Å and the H-C-H bond angle of 109.5°. The reliability

Table II. Comparison of observed and calculated structure factors for poly(ethylene succinate)

<i>hkl</i>	$\sqrt{mF_o^2}$	$\sqrt{mF_c^2}$	<i>hkl</i>	$\sqrt{mF_o^2}$	$\sqrt{mF_c^2}$	<i>hkl</i>	$\sqrt{mF_o^2}$	$\sqrt{mF_c^2}$	<i>hkl</i>	$\sqrt{mF_o^2}$	$\sqrt{mF_c^2}$
020	15.1	10.7	231	—	1.3	252	—	—	063	—	—
120	118.4	118.9	141	22.3	20.1	412	21.4	23.9	423	15.0	18.2
200	83.3	88.6	301			342			163		
220	29.2	35.1	311	—	1.3	062	14.2	16.9	433	3.0	4.6
040	26.5	27.0	321	26.2	27.5	422			353		
140	11.5	7.5	241	—	7.4	162	13.6	12.2	263	13.0	6.6
320	21.0	18.1	151	11.8	14.5	432			—		
240	8.0	10.4	331			353	18.0	19.0	503	—	3.0
400	25.1	23.5	251	9.2	11.8	262	13.0	10.8	173	10.0	7.1
340	23.5	25.9	411			442			513		
060	18.6	21.1	341	21.5	18.0	172	—	2.3	114	8.4	13.9
420			061	18.6	20.9	512	—	7.3	024	—	1.2
160	14.6	14.5	421	17.5	15.2	362	11.5	9.3	124	22.4	23.8
260	21.9	19.1	161			522			204	13.4	14.1
440	—	1.3	431	—	4.8	272	21.0	24.7	214	21.2	21.6
360	22.0	15.6	351	—	3.3	452			134	9.5	9.1
520			261	—	7.1	103	—	4.0	224		
080	—	0.7	441	—	3.9	113	—	3.8	044	11.4	6.2
180	23.4	23.3	501	—	0.9	023	7.0	7.5	234	—	7.9
540			112	21.0	27.6	123	6.0	5.9	144	17.3	18.1
460	16.1	13.0	022	9.1	8.2	213	19.8	24.9	314		
280	13.7	12.1	122	27.9	33.0	133	23.5	30.3	324	—	2.5
600			202	9.5	11.8	223			244	—	8.5
620	—	3.7	212	14.0	19.1	043	16.4	16.4	154	—	2.6
380	20.4	22.9	132	19.8	18.1	233	—	3.4	334	—	19.8
560	10.0	7.7	222	10.0	9.5	143	19.8	19.1	404	—	9.1
640			042	34.8	57.4	303			254		
101	10.8	8.7	232	30.5	30.4	313	—	3.8	414	18.1	19.8
111	19.6	14.1	142			323	—	6.2	344		
021	—	6.6	312	—	6.5	243	—	2.3	064	—	9.1
121	57.0	49.1	322	15.7	15.9	153	19.4	17.2	424	—	19.1
211	32.6	35.7	242	25.0	25.5	333			002	18.0	63.4
131	28.3	33.5	152	23.0	28.2	253	17.5	14.8	004	70.5	7.5
221	29.6	31.0	332			413			006	10.2	
041	—	5.6	402	—	5.0	343	—	—	—	—	—

factor ($\sum |\sqrt{mF_o^2} - \sqrt{mF_c^2}| / \sum \sqrt{mF_o^2}$; m , multiplicity of reflection in the fiber photograph; F , structure factor) was finally improved to 13%. Table I shows the final atomic coordinates and thermal parameters. The observed and calculated structure factors are listed in Table II. The reflection intensities of the layer lines higher than the 5-th layer line were examined qualitatively, and quite close agreement between observed and calculated intensities was found.

PEO. The observed fibre period of 11.93 Å does not fit with the calculated one, 7.20 Å, based on the zigzag planar conformation. Accordingly we assumed that the unit cell contains two molecular chains constructing the fiber period by two chemical repeating units. Here several kinds of chain conformation were possible, *i.e.*, $(TGT\bar{G})_3$, $T_5GT_5\bar{G}$, and $(TG)_6$, which can satisfy approximately the observed fibre period. But a plausible molecular model could be selected from consideration of the symmetry elements of the molecular models and the space group Pbcn. Namely, from the requirement of the space group, the molecular chain must have centers of symmetry and twofold rotation axes perpendicular to the chain axis (c axis), since the number of general equivalent positions of this space group

is eight as shown in Figure 5. Moreover from the geometrical aspect, the centers of symmetry must coincide with the midpoints of the C(O)-C(O) bonds or of the C(H₂)-C(H₂) bonds. The first case is reasonable, because in the latter case the C(O)-C(O) bonds must take *gauche* form which is apparently feasible. Accordingly it is only possible to make such a model by the conformation of $T_5GT_5\bar{G}$. The calculated fiber period based on the assumption: C-C, 1.53 Å; C(H₂)-O, 1.43 Å; C(O)-O, 1.36 Å and all skeletal bond angles are 109.5°, is 12.15 Å. The calculated fibre period is still 0.22 Å longer than the observed one. It will be possible to explain this discrepancy as a departure of the internal rotation angles from exact *trans* or *gauche* form.

The observed intensities and calculated intensities from this model showed quite close agreement. But owing to the poor orientation of the fibre sample, the refinement was carried out chiefly by using the powder data. After trial and error procedures the reliability factor ($\sum |I_o - I_c| / \sum I_o$; I_o , intensity in powder data corrected by Lorentz-polarization factor) was improved to 18%. Table III lists the atomic coordinates and thermal parameters. The observed and calculated intensities are tabulated

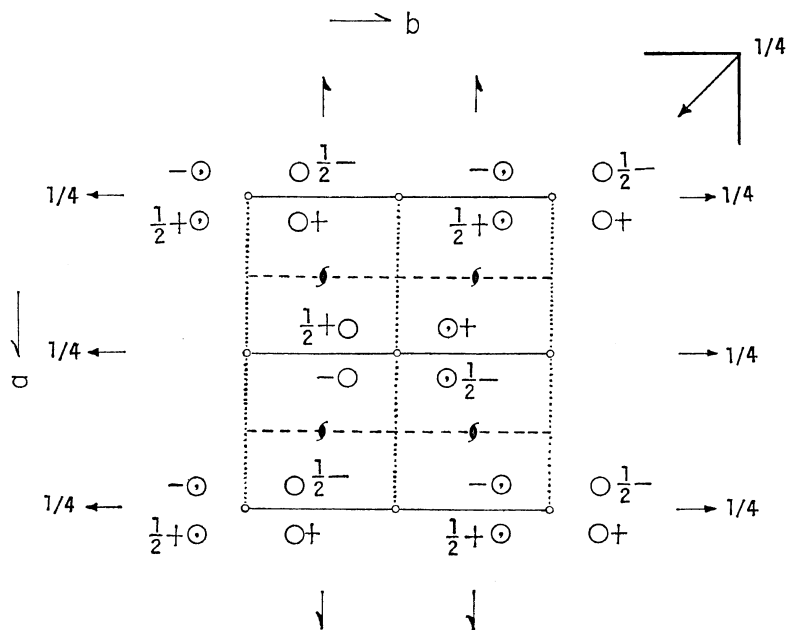


Figure 5. Equivalent positions in the space group $Pbcn-D_{2h}^{14}$ for poly(ethylene oxalate).

in Table IV.

Table III. Atomic coordinates and thermal parameters of poly(ethylene oxalate)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
C(2) ^a	-0.050	-0.304	0.308	5.0
C(3)	-0.031	-0.105	0.472	5.0
O(3)	-0.128	-0.244	0.525	7.0
O(2)	0.027	-0.117	0.364	5.0
H(1)	0.002	-0.445	0.355	7.0
H(2)	-0.281	-0.300	0.302	7.0

^a As to the numbers in parentheses, see Figures 7 and 10.

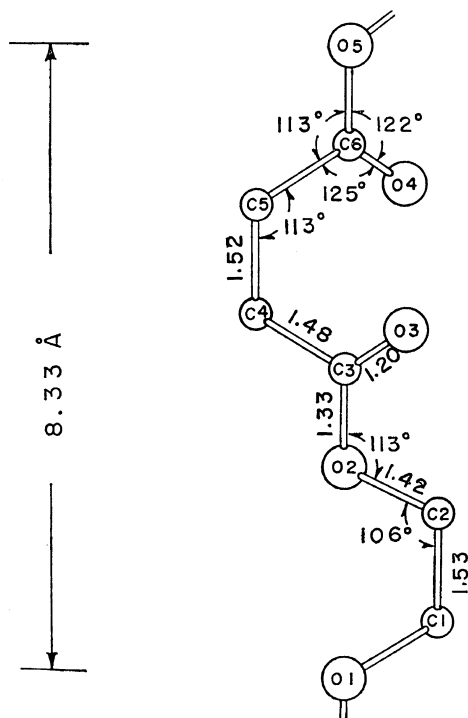
Table IV. Comparison of observed and calculated intensities for poly(ethylene oxalate)

<i>hkl</i>	<i>I</i> _o	<i>I</i> _c	<i>hkl</i>	<i>I</i> _o	<i>I</i> _c
002	240	220	214		28
110	560	537	302		10
102	—	10	124	640	112
111	1218	1296	310		120
112	252	336	006		190
200	840	890	311		254
020	238	283	130		26
021	—	51	223		229
004	—	19	131	620	82
113	—	0	312		36
202	—	1	106		0
211	1008	{748	025		16
022		35	132		84
121	—	0	215		290
104	70	89	313	408	89
212	—	44	125		0
122	—	2	116		37
114	476	{41	133		264
023		259	321		1
213	224	{282	304	600	17
123		80	231		141
221		{104	322		1
204		51	232		28
024	710	{121			
115		280			
222		54			

RESULT AND DISCUSSION

Molecular Conformation

Figures 6 and 7 show the molecular dimensions of PES and PEO, respectively. No abnormal bond lengths and angles are found when compared with other esters. The accuracy of the molecular dimensions of PEO may be slightly less than those of PES. The molecular conformation of PES and PEO are essentially T₃GT₃Ḡ and T₅GT₅Ḡ, respectively. The internal rotation angles about the bonds in the skeletal chain of PES and PEO are shown in Table V. The similarity in both molecular conformations is that all the C(H₂)-C(H₂) bonds are of *gauche* form and all other bonds are *trans* form. It should be emphasized these conformations are quite different from those of higher members (*y* ≥ 4), in which the CH₂ sequences have planar carbon chains but the C(H₂)-O bond is of *skew* form (S), as already discovered in detail by Turner-Jones and Bunn.⁸ Figure 8 shows the length of the chemical repeating unit along the fiber axis for the polyesters of the ethylene glycol series.

**Figure 6.** Bond lengths and bond angles of poly(ethylene succinate).

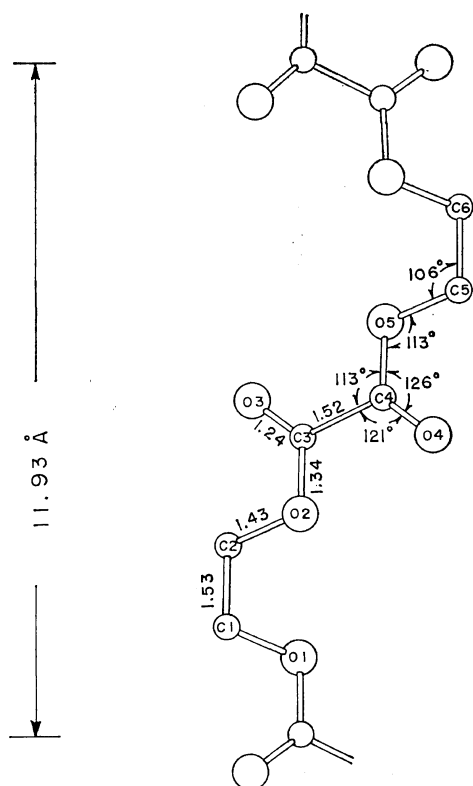


Figure 7. Bond lengths and bond angles of poly(ethylene oxalate).

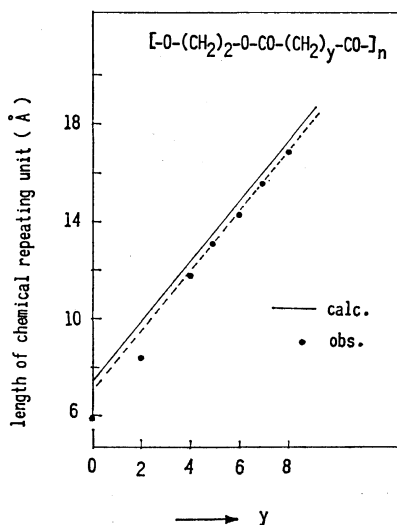
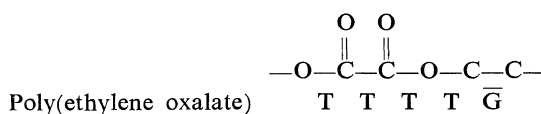
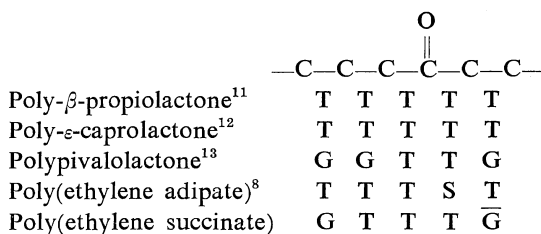


Figure 8. Lengths of chemical repeating units of the ethylene glycolic series polyesters against number of methylene groups of acid parts.

Table V. Internal rotation angles

Poly(ethylene succinate)		Poly(ethylene oxalate)	
C(1)-C(2)	-77°	C(1)-C(2)	-64°
C(2)-O(2)	175°	C(2)-O(2)	174°
O(2)-C(3)	176°	O(2)-C(3)	174°
C(3)-C(4)	176°	C(3)-C(4)	180°
C(4)-C(5)	65°		

The shortening of about 0.5 Å from the extended forms in the higher members ($y \geq 4$) is due to the *skew* form of the $C(H_2)-O$ bond, while the shortening of about 1.45 Å in PES and PEO is attributed to the *gauche* form of the $C(H_2)-C(H_2)$ bonds. Summarizing the skeletal conformations of some polyesters analyzed so far, there seem to be some features concerning internal rotation which should be noted.



In these polyesters the $C(O)-O$ bonds are *trans*, and the $C(O)-C$ bonds are also *trans*, except for polypivalolactone in which two methyl groups are attached to the carbon atom instead of hydrogen atoms. Therefore the $C(O)-O$ and $C(O)-C$ bonds are stable in the *trans* form so long as no large substituent groups are introduced. The $O-C$ bonds also preferably take the *trans* form, whereas in the ethylene glycol series, the $C-C$ bond of the glycol part takes either the *trans* or *gauche* form.

Crystal Structure

In the polyesters of the ethylene glycol series, it is well known that the odd members of $y \geq 5$ are of orthorhombic form and the even members of $y \geq 4$ occur in monoclinic form. However, the lateral chain packings of these polyesters are essentially of the polyethylene type. On the other hand the PES and PEO crystals take

Poly(ethylene succinate) and Poly(ethylene oxalate)

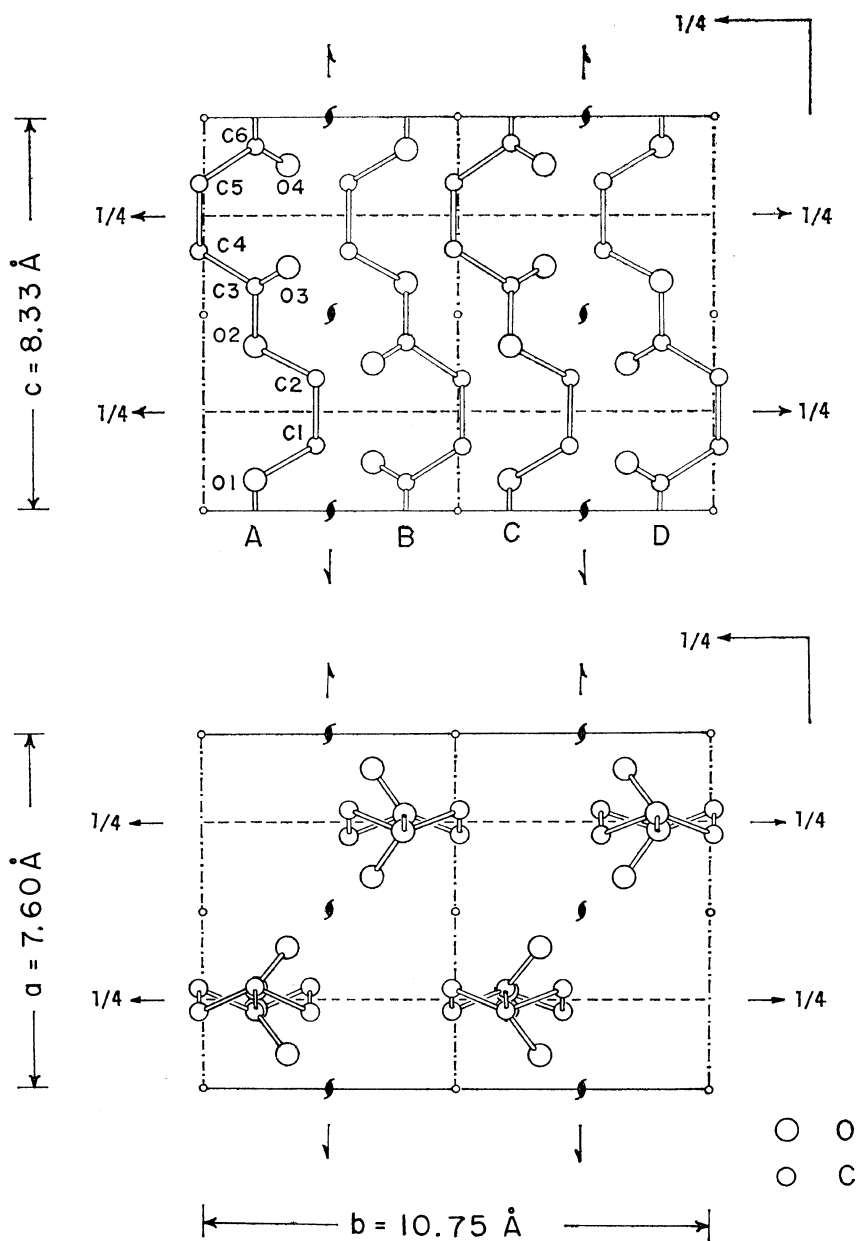


Figure 9. Crystal structure of poly(ethylene succinate).

layer structures parallel to the b axis, as shown in Figures 9 and 10. The PES molecules have twofold rotation axes which fit the twofold rotation axes along the b axis at $z=1/4$ and $3/4$. As can be seen from Figure 9, the dipole moment vector in each molecule is oriented in one direction at $z=1/4$, and in the opposite direction at

$z=3/4$. Such a dipole arrangement seems to stabilize the crystal lattice and hence to contribute to the high melting point of this polymer. The interatomic distances are tabulated in Table VI. In the case of PEO, the concentration of ester groups is greatest in the homologous series. The cohesive energy due to the dipole interaction

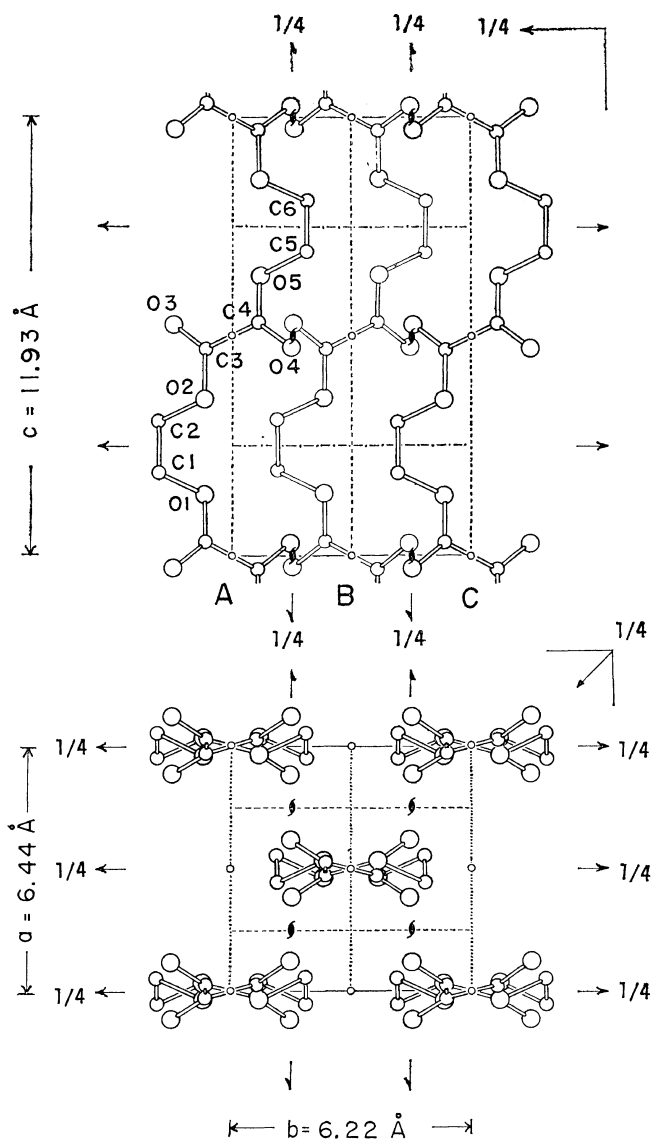


Figure 10. Crystal structure of poly(ethylene oxalate).

Table VI. Interchain atomic distances

Poly(ethylene succinate)		Poly(ethylene oxalate)	
C(1, A).....O(3, B)	3.27 Å	O(4, A).....C(3, B)	2.71 Å
C(2, A).....O(3, B)	3.39 Å	O(4, A).....O(2, B)	2.71 Å
C(5, C).....O(1, B)	3.56 Å	O(4, A).....C(2, B)	3.34 Å
C(2, B).....C(5, C)	4.02 Å	O(4, A).....C(2, C)	3.60 Å
C(4, B).....C(2, C)	4.09 Å	C(5, A).....O(5, B)	3.69 Å
C(2, A).....C(4, C)	4.16 Å	C(5, A).....C(5, B)	4.04 Å

is therefore greatly increased. It seems probable that as the number of methylene groups increases, inter and intrachain methylene—methylene interactions become more likely and the molecules tend to pack in a manner similar to polyethylene.

According to a thermodynamical study by Hobbs and Billmeyer, Jr.¹⁴ on poly(ethylene adipate) ($y=4$), poly(ethylene suberate) ($y=6$) and poly(ethylene sebacate) ($y=8$), heats of fusion (ΔH_f) and entropies of fusion (ΔS_f) per mole of backbone atoms show a gradual decrease with decreased ester group spacing, *i.e.*, ΔH_f , 502, 527, and 546 cal/(mol of backbone) for $y=4$, 6, and 8, respectively; ΔS_f , 1.48, 15.0, and 1.54 cal/(mol of backbone °C) for $y=4$, 6, and 8, respectively. But reductions in the entropies of fusion of the polyesters are overcompensated by more substantial decreases in their heats of fusion. Therefore the melting points of the polyesters decrease with decreased ester group spacing. These three polyesters are isomorphous in their chain conformation and lateral chain packing structures (polyethylene-like). From these facts it seems likely that entropies of fusion of PES ($y=2$) and PEO ($y=0$) might be smaller than those of the higher members of y , and in particular the entropy of fusion of PEO must be smaller due to the $-\text{CO}-\text{CO}-$ bond. On the other hand, with respect to the crystal structures of PES and PEO determined in this study, it is presumed that heats of fusion of PES and PEO increase and that as a result PES and PEO have high melting points of 112 and 172°C, respectively.

Acknowledgment. The authors would like to thank Dr. M. Kobayashi and Mr. K. Tai for supplying information on infrared studies and for helpful discussions. The authors also wish to thank Mr. K. Suehiro for his assistance in the earlier stages of structural analyses.

REFERENCES

1. C. S. Fuller and C. L. Erickson, *J. Amer. Chem. Soc.*, **59**, 344 (1937).
2. C. S. Fuller and C. J. Frosch, *J. Phys. Chem.*, **43**, 323 (1939).
3. C. S. Fuller, *Chem. Rev.*, **26**, 143 (1940).
4. C. S. Fuller, C. J. Frosch, and N. R. Pape, *J. Amer. Chem. Soc.*, **64**, 154 (1942).
5. C. W. Bunn, *Trans. Faraday Soc.*, **35**, 482 (1939).
6. C. W. Bunn, *Proc. Roy. Soc.*, **A180**, 67 (1952).
7. W.H. Carothers, J. A. Arvin, and G. L. Dorouch, *J. Amer. Chem. Soc.*, **52**, 3292 (1930).
8. A. Turner-Jones and C. W. Bunn, *Acta Cryst.*, **15**, 105 (1962).
9. H. Tadokoro, M. Kobayashi, H. Yoshidome, K. Tai, and D. Makino, *J. Chem. Phys.*, **49**, 3359 (1968).
10. K. Tai, M. Kobayashi, and H. Tadokoro, unpublished data.
11. A. S. Ueda, Y. Chatani, and H. Tadokoro, to be published.
12. Y. Chatani, Y. Okita, H. Tadokoro, and Y. Yamashita, *Polymer J.*, **1**, 555 (1970).
13. G. Carazzolo, *Chim. Ind. (Milano)*, **46**, 525 (1964).
14. S. Y. Hobbs and F. W. Billmeyer, Jr., *J. Polym. Sci., Part A-2*, **8**, 1387 (1970).