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Crystal Structure of Poly(trimethylene carbonate)

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ABSTRACT: Poly(trimethylene carbonate) (PTrMC) is a member of poly(alkylene carbonate) represented by the chemical formula $[-(CH_2)_mOC{=}OO-]_n$. PTrMC is found to be a synthetic rubber, which is amorphous in the relaxed state and crystalline in the stretched state. PTrMC can be synthesized enzymatically and therefore can be called a biodegradable elastomer. In the present study, the crystal structure analysis of PTrMC was carried out using an imaging plate by the X-ray diffraction method. Two molecular chains pass through a unit cell with parameters $a = 7.02$ Å, $b = 5.81$ Å, and c(fiber axis) = 12.30 Å and the space group $P2_1cn-C_{2v}^9$. The molecules assume the $\bar{S}TST_2GST\bar{S}T_2\bar{G}$ conformation distorted from $T_5GT_5\bar{G}$.

Introduction

Poly(trimethylene carbonate) (PTrMC) $[-CH_2CH_2CH_2OC({=}O)O-]_n$ is the third member ($m = 3$) of a series of poly(alkylene carbonate)s represented by the general formula $[-(CH_2)_m-OC({=}O)O-]_n$. PTrMC is synthesized by the ring-opening polymerization of 1,3-dioxan-2-one (trimethylene carbonate).[1,2] Recently, PTrMC is also reported to be polymerizable enzymatically.[3] Accordingly, PTrMC is a biodegradable polymer. In the present study, PTrMC is shown to be a synthetic rubber, an elastomer, which is amorphous in the relaxed state and crystalline in the stretched state. Therefore, PTrMC is concluded to be a biodegradable elastomer. In the present study, the crystal structure of PTrMC in a stretched state is clarified by using the X-ray diffraction method.

Experimental Section

X-ray measurements were carried out by using Cu Kα radiation monochromatized by a pyrolytic graphite. An imaging plate was used to record the fiber and Weissenberg diagrams and read the intensities digitally by R-AXIS DSS (Rigaku Denki Co. Ltd.). The fiber diagrams were taken by a cylindrical camera with 5 cm radius in He gas stream (Figure 1). The Weissenberg diagrams were taken by a camera with 4.5 cm radius according to Norman's method.[4] A Weissenberg diagram is shown in Figure 2 along with a schematic representation.

The sample was kindly supplied by Prof. Kricheldorf. The sample was first casted on the glass plate from a 10% chloroform solution, which was stretched about 3 times and fixed on the metal holder. After keeping the specimen at −20 °C for 3 months, it served to the X-ray experiments. The sample thus obtained is doubly oriented, and therefore, the fiber diagrams were taken by rotating the sample around the fiber axis. Integrated intensities were estimated by the following procedures (Figure 3),[5] in the same way as by the drum scan densitometer procedures of the X-ray film.[6−8] First, the digital data for one pixel (100 μm^2) of the reflection are summed up along the arc with constant 2θ, and the summed intensities are plotted against a layer line. And, from the one-dimensional intensity curve thus obtained, the integrated intensity was estimated. Here, for the overlapped reflections, one-dimensional intensity curve was fitted and separated under the assumption of a pseudo-Voigt function: a linear combination of Gauss and Cauchy functions.

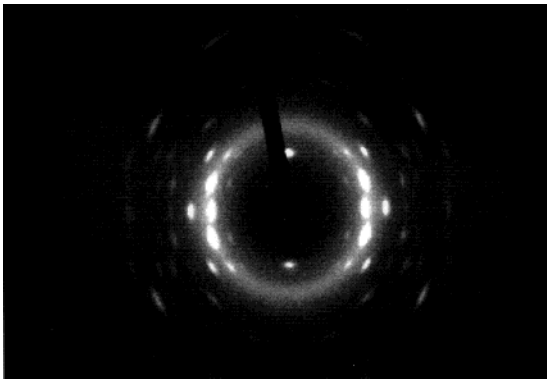
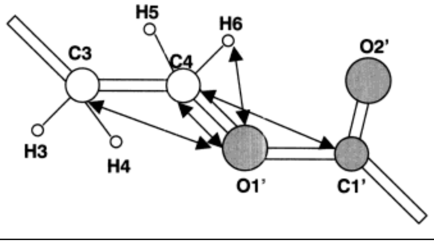


Figure 1. Fiber diagram of PTrMC taken by an imaging plate.

Table 1. Bond Lengths (Å) and Bond Angles (deg) Fixed during the Refinements

C−C	1.54	C−C−C	110.0
C−O	1.43	C−C−O	110.0
C−H	1.09	C−O−C	110.0
C═O	1.24	O−C−O	120.0

Table 2. Interatomic Distances (Å) Fixed by Lagrange's Undetermined Multipliers



Constrained condition (Å)	
C3−O1′	2.4336
C4−O1′	1.4300
H6−O1′	2.0517
C4−O1′	2.3428

Results and Discussion

Elasticity. PTrMC is amorphous in an unstretched state (Figure 4a); but when the sample is stretched, PTrMC crystallizes under tension (Figure 4b), and when the tension is relaxed, PTrMC becomes amorphous. This

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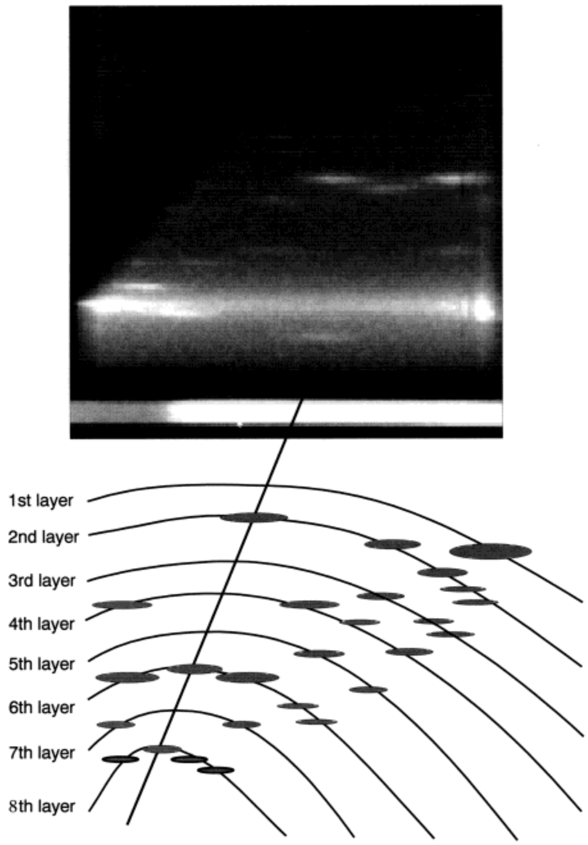


Figure 2. Weissenberg diagram and its schematic representation.

Table 3. Final Parameters Obtained by the Constrained Least-Squares Refinement

	values	SD[a]
fractional coordinates of the origin atom O1[b]		
y(O1)	0.134	0.007
z(O1)	0.018	0.005
Euleiran angles (deg)		
θ	−120.9	1.7
φ	−26.0	2.6
χ	51.6	1.2
internal rotation angles (deg)		
O1−C1−O3−C2	156.4	3.9
C1−O3−C2−C3	181.4	3.8
O3−C2−C3−C4	65.6	3.7
C2−C3−C4−H	−4.0	5.4
temperature parameters (Å^2)		
B(O1)	7.9	3.8
B(C1)	3.4	2.2
B(O2)	14.5	3.3
B(O3)	9.0	2.3
B(C3)	1.4	1.4
B(C4)	3.5	2.3

[a] Standard deviations. [b] Numbering of atoms are given as follows: −O1C1(=O2)O3C2C3C4−.

phenomenon can be generally seen in the case of elastomer including natural rubber. Accordingly, PTrMC can be called an elstomer. However, the sample of high crystallinity does not shrink and is still crystalline in a relaxed state.

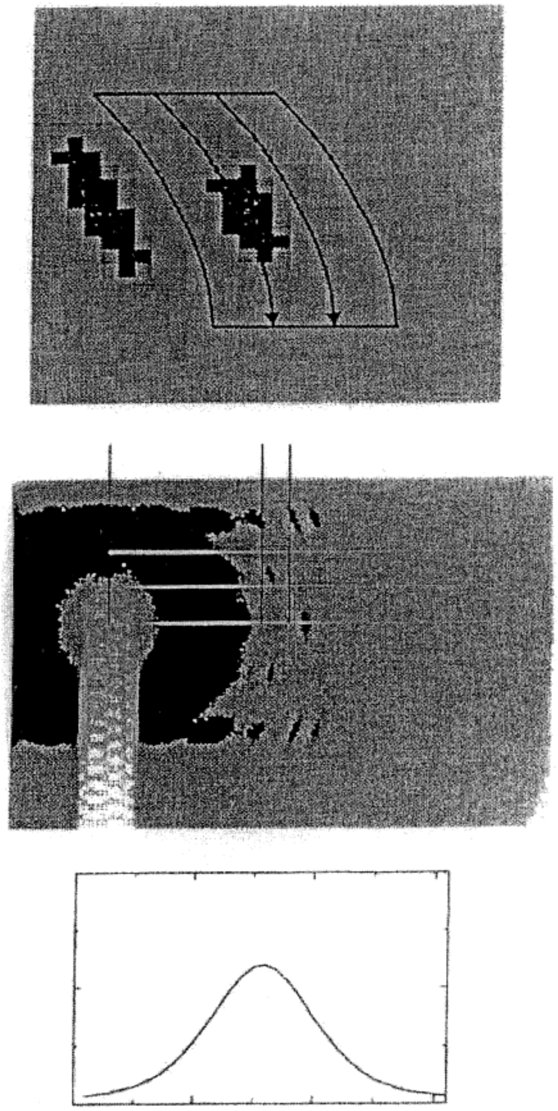


Figure 3. Schematic representation for estimation of integrated intensities.

Table 4. Final Atomic Parameters in Fractional Coordinates

atom	*x*	*y*	*z*
O1	0.000	0.134	0.018
C1	0.012	0.341	0.080
O2	0.114	0.502	0.048
O3	−0.094	0.364	0.178
C2	−0.007	0.532	0.247
H1	0.139	0.483	0.265
H2	−0.006	0.699	0.207
C3	−0.118	0.552	0.355
H3	−0.060	0.692	0.404
H4	−0.268	0.587	0.338
C4	−0.102	0.326	0.419
H5	−0.244	0.259	0.437
H6	−0.025	0.198	0.372

Unit Cell Dimensions and Molecular Models. All the observed reflections can be indexed by an orthorhombic unit cell with parameters *a* = 7.02 Å, *b* = 5.81 Å, and *c*(fiber axis) = 12.30 Å. From the fiber period 12.30 Å, two molecular models can be considered, which are shown in Figure 5. First, one is the $T_5GT_5\bar{G}$ conformation, in which one of two C−C bonds assumes the G or $\bar{G}$ conformation. The calculated fiber identity period is 12.67 Å. Another model is the $(T_4G_2)_2$ (the calculated fiber identity period: 10.28 Å), in which two C−C bonds assume the G conformation. Assuming two molecular chains in the unit cell, the calculated density is 1.351 g/cm^3, which is in good agreement with the observed density 1.365 g/cm^3 measured by the flotation method in a methanol−carbon tetrachloride mixture.

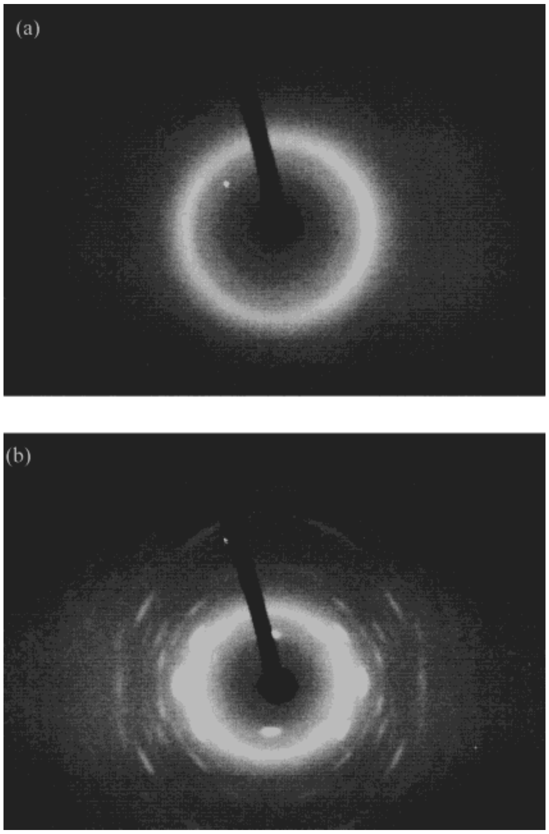


Figure 4. Fiber diagrams of PTrMC (a) in a relaxed state and (b) in a stretched state.

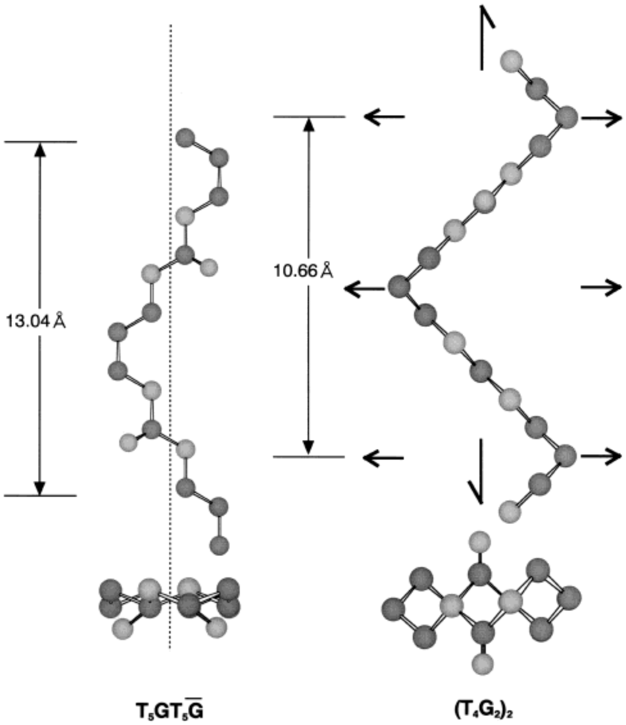


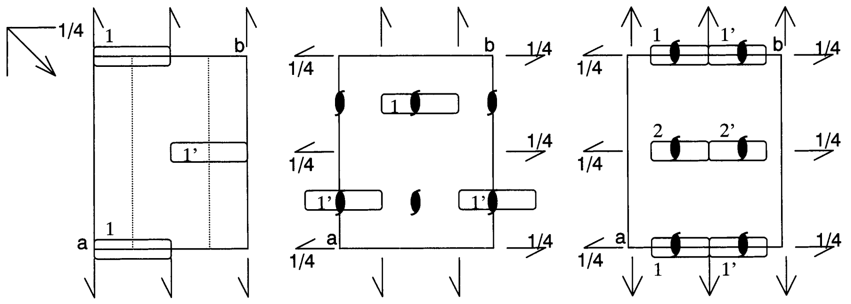
Figure 5. Two possible molecular models for PTrMC.

Table 5. Comparison between Observed and Calculated Structure Factors

h	k	l	$I_{ob}^{1/2}$	$I_c^{1/2}$	h	k	l	$I_{ob}^{1/2}$	$I_c^{1/2}$
1	1	0	62.9	66.9	3	3	2	7.0	7.0
2	0	0	66.7	70.6	4	4	2		
0	2	0	10.1	17.0	1	4	2		
2	2	0	8.7	11.4	0	4	2	9.4	11.1
3	1	0	29.8	21.4	4	0	2		
1	3	0	8.6	7.6	0	1	3	21.8	13.2
4	0	0	10.7	13.2	1	1	3		
4	2	0	9.7	11.2	2	1	3	15.3	14.1
3	3	0			0	2	3		14.6
0	4	0		6.8	1	2	3	37.2	37.4
5	1	0	8.5	10.0	2	2	3		
2	4	0			3	1	3	12.4	19.2
6	0	0			0	3	3	22.2	18.8
5	3	0	25.2	25.2	1	3	3		17.7
1	5	0			3	2	3	15.6	16.1
4	4	0			2	3	3	19.5	17.7
0	1	1	6.3	9.0	4	1	3		
1	1	1	84.0	79.1	3	3	3	9.5	12.5
2	1	1	24.2	34.7	4	2	3		
0	2	1		11.9	1	0	4	29.2	23.7
1	2	1	6.2	7.9	0	1	4	14.0	12.6
2	2	1			1	1	4	11.8	8.0
3	1	1	20.8	24.0	2	0	4		24.3
0	3	1			2	1	4		29.4
1	3	1	8.0	9.1	0	2	4		7.9
2	3	1			1	2	4	15.4	15.7
4	1	1	11.6	8.1	3	0	4		21.3
3	2	1			2	2	4		
4	2	1		4.5	3	1	4	11.0	14.2
3	3	1		5.6	0	3	4		
0	4	1		14.0	1	3	4	17.0	15.8
1	4	1	8.2	9.4	3	2	4		
5	1	1		7.5	4	0	4		
2	4	1		13.6	2	3	4	13.4	15.4
4	3	1		6.7	0	1	5	12.5	5.2
3	4	1	10.4	13.2	1	1	5	36.5	24.0
5	2	1			0	2	5		
1	0	2	29.2	30.0	2	1	5	16.9	16.0
0	1	2	22.1	19.3	1	2	5		10.9
1	1	2	37.4	26.5	2	2	5		
2	0	2	13.1	20.5	3	1	5	19.3	19.6
2	1	2	20.6	17.1	1	0	6		
0	2	2	7.7	11.4	0	1	6	25.5	26.3
1	2	2	14.1	10.6	1	1	6		
3	0	2		21.2	2	0	6		
2	2	2	18.7	19.4	2	1	6		
3	1	2	13.9	14.5	0	2	6		
3	2	2	9.8	9.2	1	2	6	22.4	17.9
1	3	2			3	0	6		
2	3	2	12.8	16.8	2	2	6		
4	1	2			3	1	6		

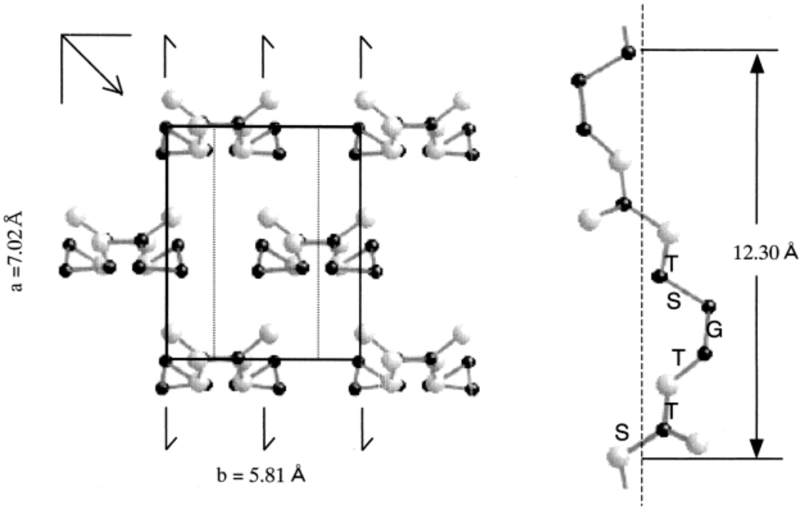
Space Group. The systematic absences $h + k = 2n + 1$ for $hk0$ and $l = 2n + 1$ for $h0l$ were found. Therefore, three possible space groups, $P2_1cn{-}C_{2v}^9$, $P2_12_12_1{-}D_2^4$, and $P22_12_1{-}D_2^3$, were examined. In Figure 6, the symmetries and molecular packings in three space groups are shown. In the space group $P2_1cn{-}C_{2v}^9$, two molecular chains with the $T_5GT_5\bar{G}$ conformation are located on the glide symmetries of the space group. In the space group $P2_12_12_1$, two molecular chains with $(T_4G_2)_2$ conformation are located on the 2-fold screw axes of the space group. And in the space group $P22_12_1{-}D_2^3$, two molecular chains with the $(T_4G_2)_2$ conformation are also located on the 2-fold screw axes of the space group. After the trial-and-error procedures, three crystal structure models were refined by the constrained least-squares method.[8,10]

Refinements. Refinements were carried out by the constrained least-squares method.[10,11] During the refinements, the bond lengths and bond angles were fixed on the accepted values given in Table 1. The bond lengths and bond angles between two chemical units were fixed by keeping the interatomic distances in the values given in Table 2 by the Lagrange undetermined multipliers. Refinements for the space groups $P2_12_12_1$ and $P22_12_1$ with the $(T_4G_2)_2$ conformation did not converge to the R-factors less than 26%. Only the space



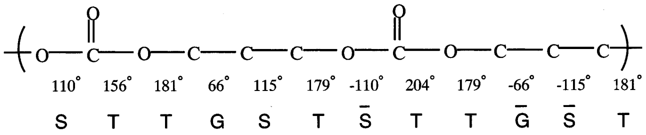
$P2_1cn$ $P2_12_12_1$ $P22_12_1$

Figure 6. Symmetries and molecular packings in three space groups.



(a) (b)

Figure 7. Crystal structure of PTrMC.



$$-\!\!\!\left(O-\overset{\overset{O}{\|}}{C}-O-C-C-C-O-\overset{\overset{O}{\|}}{C}-O-C-C-C\right)\!\!\!-$$

Figure 8. Internal rotation angles of the single bonds.

group $P2_1cn$ converged to the R-factor 16.8%. Here, the refined parameters are the fractional coordinates of the origin carbon atom O1, Eulerian angles θ, φ, and χ, internal rotation angles O1−C1−O3−C2, C1−O3−C2−C3, O3−C2−C3−C4, and C2−C3−C4−H, and isotropic temperature parameters B(O1), B(C1), B(O2), B(O3), B(C3), and B(C4). The isotropic temperature parameters of the C2 atom and hydrogen atoms were fixed on 8.5 and 9.5 Å^2, respectively. The crystal structure is shown in Figure 7. Final parameters obtained by the constrained least-squares refinement and in fractional coordinates are given in Tables 3 and 4, respectively. A comparison between the observed and calculated structure factors is given in Table 5.

Molecular and Crystal Structures. The internal rotation angles around the single bonds are shown in Figure 8. Two neighboring C−C bonds assume G and S conformations. The S conformation around the C−C single bond is seen in the cases of poly(1,3-dioxolane) form II,[11] poly(*tert*-butylethylene oxide),[12] and poly(isopropylethylene oxide).[13] Interatomic distances between two neighboring molecules are shown in Figure 9. The distance 2.772 Å between carbonyl oxygen and carbon atoms is slightly shorter than the sum of the van der Waals radii. This may be attributed to the assumption of the accepted bond lengths and bond angles, and it may be suggested that the carbonyl oxygen atom may be distorted from the plane of O−(C=O)−O.

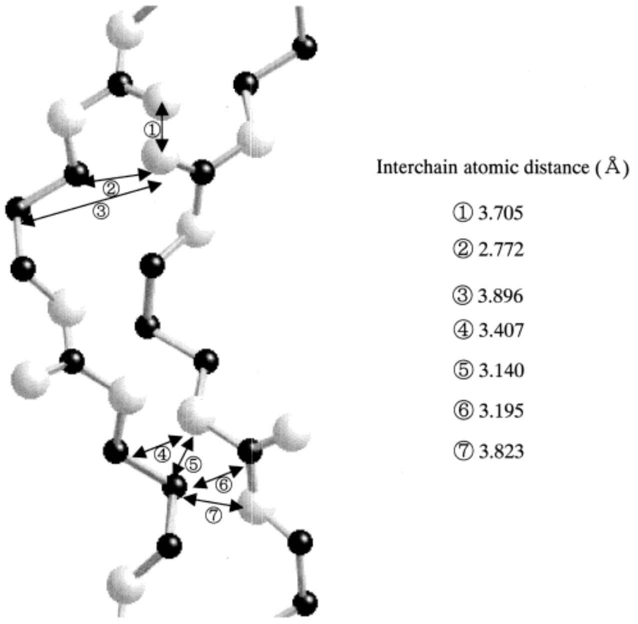


Figure 9. Interatomic distances between the neighboring molecules.

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