

Fundamentals of Crystallography (A survey of  
polymer crystallization by X-ray diffraction .  
chapter 1)

|       |   |
|-------|---|
| メタデータ | 言語: en<br>出版者: SKP<br>公開日: 2008-01-31<br>キーワード (Ja):<br>キーワード (En):<br>作成者: Asano, Tsutomu, Mina, Md. Forhad<br>メールアドレス:<br>所属: |
| URL   | <a href="http://hdl.handle.net/10297/548">http://hdl.handle.net/10297/548</a>   |

# Chapter 1. Fundamentals of Crystallography

## 1.1. Crystal Structure

In solids, atoms are rigidly held together by mutual interactions commonly known as covalent, ionic, metallic, van der Waals and hydrogen bonds. A crystal is a solid within which atoms are arranged in a regular, repeated and three-dimensionally periodic way by the aforesaid interactions. The atoms or molecules in a crystal are called structural units. An ideal crystal is constructed by the infinite repetition of the identical structural units. Concept of the regular arrangement is represented by a lattice, having periodic points in a space. The lattice is formed by three translational vectors  $\mathbf{a}$ ,  $\mathbf{b}$  and  $\mathbf{c}$ . Then, the crystal lattice vector in a real space,  $\mathbf{r}$ , is defined by

$$\mathbf{r} = p\mathbf{a} + q\mathbf{b} + r\mathbf{c}, \dots \dots \dots (1.1)$$

where,  $p$ ,  $q$  and  $r$  are integers. For simplicity, we refer to Fig.1.1 for a two-dimensional representation of  $\mathbf{r}$  in terms of  $\mathbf{a}$  and  $\mathbf{b}$ . The position defined by  $\mathbf{r}$  from the origin (O) has identical surroundings by the translational operation.

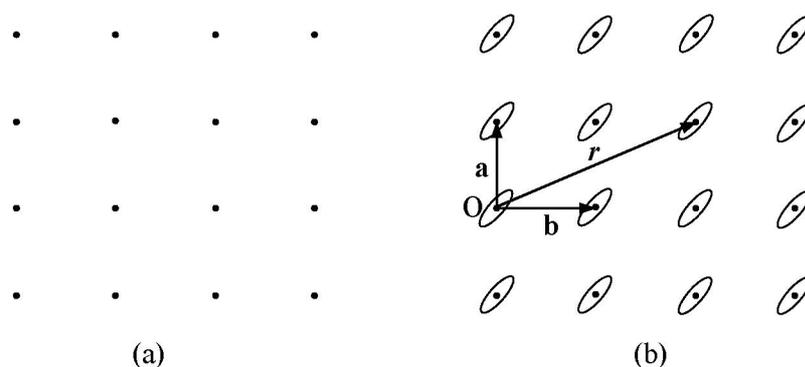


Fig.1.1 (a) Lattice points and (b) crystal lattice vector in two dimensions, where atoms or molecules are attached to each lattice point.

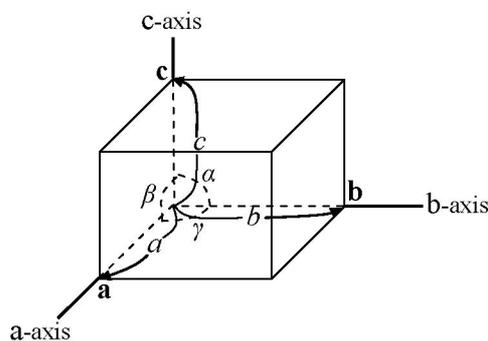


Fig. 1. 2 A set of axes, showing definitions of  $a$ ,  $b$ ,  $c$  and  $\alpha$ ,  $\beta$ ,  $\gamma$ .

The parallelepiped defined by the crystalline axes is called a primitive cell or unit cell. In Fig.1.2,  $a$ ,  $b$  and  $c$  are the repeating distances along the three crystalline axes ( $a$ ,  $b$  and  $c$ ), and  $\alpha$ ,  $\beta$  and  $\gamma$  are angles between the axes. These parameters are called crystallographic parameters. Due to the periodic arrangement of atoms, crystals exhibit anisotropic properties. Depending on the atomic or molecular arrangements, crystals also exhibit symmetry. By the symmetry operations such as rotation and reflection, the crystal structure is possible to superpose on itself. Considering a three-dimensional symmetry in space, natural crystals are classified into seven crystal systems. Bravais showed that, there are 14 fundamental lattices, called Bravais lattice or space lattice [1]. The seven crystal systems and the crystallographic parameters are shown in Table 1.1.

Table 1.1 Crystal systems

| Crystal System | Axes              | Axial angles   |
|----------------|-------------------|--|
| Cubic          | $a = b = c$       | $\alpha = \beta = \gamma = 90^\circ$                 |
| Hexagonal      | $a = b \neq c$    | $\alpha = \beta = 90^\circ, \gamma = 120^\circ$      |
| Trigonal       | $a = b = c$       | $\alpha = \beta = \gamma < 120^\circ, \neq 90^\circ$ |
| Tetragonal     | $a = b \neq c$    | $\alpha = \beta = \gamma = 90^\circ$                 |
| Orthorhombic   | $a \neq b \neq c$ | $\alpha = \beta = \gamma = 90^\circ$                 |
| Monoclinic     | $a \neq b \neq c$ | $\alpha = \gamma = 90^\circ \neq \beta$              |
| Triclinic      | $a \neq b \neq c$ | $\alpha \neq \beta \neq \gamma \neq 90^\circ$        |

Historically, the German physicist Max von Laue first suggested in 1912 that X-rays could be diffracted by crystals [2]. Owing to its wavelength comparable to inter-atomic distances, X-ray is possible to be diffracted by a crystal. This property of X-ray is basically used for studying crystalline structures and arrangements of molecules.

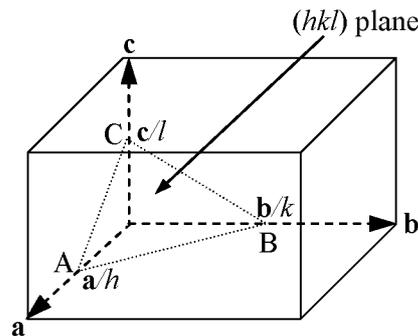


Fig.1.3 Unit cell and  $(hkl)$  plane.

## 1.2. Concept of Lattice Planes

Due to their periodic arrangement along the three-axes, space lattices produce lattice planes or crystal planes. The orientation of a lattice plane can be determined by three points if they are not collinear. For clarification, if we draw a unit cell of the crystal with the vectors  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$  as shown in Fig. 1.3 and if three points  $A$ ,  $B$  and  $C$  lay on different axes, then the

plane can be defined by the coordinates of the three points.

It is useful for structural analysis to specify the crystalline plane by Miller indices  $h$ ,  $k$  and  $l$ . If we assume a plane passing through the origin, then the next plane, which intersects at  $a/h$ ,  $b/k$  and  $c/l$ , is defined by the  $(hkl)$  plane as represented in Fig.1.3. Thus, the indice  $(hkl)$  denotes either a single plane or a set of parallel planes inside the crystal. Considering the repetition of the unit cell,  $h$ ,  $k$  and  $l$  become integers.

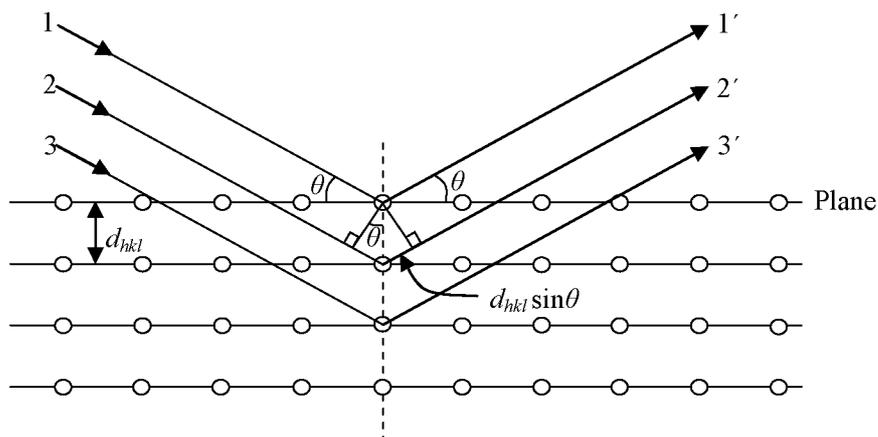


Fig. 1.4 Reflection of X-rays from a set of  $(hkl)$  planes.

### 1.3. Bragg's Condition

X-ray diffraction analysis was based on the relation of Bragg's condition developed in 1913. Figure 1.4 illustrates a set of  $(hkl)$  planes, separated by equal distance  $d_{hkl}$ , where molecules are periodically arranged. We consider parallel X-ray beams (1, 2, 3) are incident on the lattice planes at an angle,  $\theta$ . The beams undergo mirror reflection from the parallel planes, having the reflecting angle equal to  $\theta$ . If we consider elastic scattering, without changing the wavelength, the diffracted beams (1', 2', 3') will interfere under the condition of the reflection. If we consider the case of the adjacent planes, path difference between the two rays 11' and 22' becomes  $2d_{hkl} \sin \theta$ . Constructive interference occurs when the path difference of the two beams has an integral multiple of the wavelength,  $\lambda$ . Then, the constructive interference occurs when,

$$2 d_{hkl} \sin \theta = n \lambda. \dots \dots \dots (1.2)$$

This is the Bragg's law used in optics and crystallography. However, in X-ray crystallography, the plane distance  $d_{hkl}/n$  is usually generalized to be  $d_{hkl}$ , and then the above equation becomes

$$2 d_{hkl} \sin \theta = \lambda. \dots \dots \dots (1.3)$$

### 1.4 Reciprocal Lattice

The concept of 'reciprocal lattice' is very much useful to simplify the calculations of crystallographic data and to understand the theory of diffraction. Essentially, this concept has

its origin in the mathematical definition of a set of vectors, called the reciprocal lattice vectors. We have assumed that  $\mathbf{a}$ ,  $\mathbf{b}$  and  $\mathbf{c}$  are the three translation vectors in the real space that describe the shape and size of the unit cell of a particular crystal lattice. A set of the reciprocal vectors  $\mathbf{a}^*$ ,  $\mathbf{b}^*$  and  $\mathbf{c}^*$  is defined as:

$$\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}, \quad \mathbf{b}^* = \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}, \quad \mathbf{c}^* = \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} \dots\dots\dots (1.4)$$

The triple product of the denominator is equal to the volume of the unit cell of the real space. From the definition,  $\mathbf{a}^*$  is perpendicular to the plane formed by  $\mathbf{b}$  and  $\mathbf{c}$ ;  $\mathbf{b}^*$  is perpendicular to the plane formed by  $\mathbf{c}$  and  $\mathbf{a}$ , and  $\mathbf{c}^*$  is perpendicular to the plane formed by  $\mathbf{a}$  and  $\mathbf{b}$ . Then the relations between real and reciprocal vectors become:

$$\begin{array}{lll} \mathbf{a} \cdot \mathbf{a}^* = 1, & \mathbf{a} \cdot \mathbf{b}^* = 0, & \mathbf{a} \cdot \mathbf{c}^* = 0, \\ \mathbf{b} \cdot \mathbf{a}^* = 0, & \mathbf{b} \cdot \mathbf{b}^* = 1, & \mathbf{b} \cdot \mathbf{c}^* = 0, \dots\dots\dots (1.5) \\ \mathbf{c} \cdot \mathbf{a}^* = 0, & \mathbf{c} \cdot \mathbf{b}^* = 0, & \mathbf{c} \cdot \mathbf{c}^* = 1, \end{array}$$

The reciprocal vectors represent a reciprocal lattice. Dimension of the reciprocal space is reverse of length.

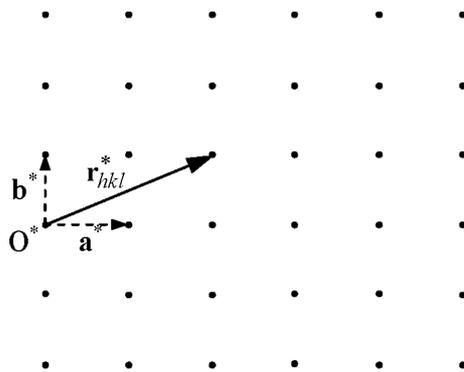


Fig. 1.5 Definition of the vector in the reciprocal space.

The reciprocal lattice vector is defined by:

$$\mathbf{r}_{hkl}^* = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \dots\dots\dots (1.6)$$

$\mathbf{r}_{hkl}^*$  is the vector from the origin ( $O^*$ ) to any lattice point in the reciprocal space (Fig.1.5), where  $h$ ,  $k$  and  $l$  are integers. We shall now establish a relation between the real and reciprocal space using  $(hkl)$  plane and  $\mathbf{r}_{hkl}^*$ . In Fig. 1.6(a), the triangle  $\Delta ABC$  is on the  $(hkl)$  plane in the real space, which intersects at points  $\mathbf{a}/h$ ,  $\mathbf{b}/k$  and  $\mathbf{c}/l$ . Using these intercepts, the vectors  $\mathbf{AB}$ ,  $\mathbf{AC}$  and  $\mathbf{CB}$  can be represented as:  $\mathbf{AB} = \mathbf{b}/k - \mathbf{a}/h$ ,  $\mathbf{AC} = \mathbf{c}/l - \mathbf{a}/h$  and  $\mathbf{CB} = \mathbf{b}/k - \mathbf{c}/l$ . Using Eq. (1.5),

$$\mathbf{r}_{hkl}^* \cdot \mathbf{AB} = (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*) \cdot (\mathbf{b}/k - \mathbf{a}/h) = (k/k - l/l) = 0$$

Similarly,  $\mathbf{r}_{hkl}^* \cdot \mathbf{AC} = 0$  and  $\mathbf{r}_{hkl}^* \cdot \mathbf{BC} = 0$ . Therefore,  $\mathbf{r}_{hkl}^*$  is perpendicular to the  $(hkl)$  plane. Let  $\mathbf{n}$  be the unit vector perpendicular to the  $(hkl)$  plane.

Then, the direction of  $\mathbf{r}_{hkl}^*$  is parallel to  $\mathbf{n}$ , and hence we can write:

$$\mathbf{r}_{hkl}^* = |\mathbf{r}_{hkl}^*| \mathbf{n} \dots\dots\dots(1.7)$$

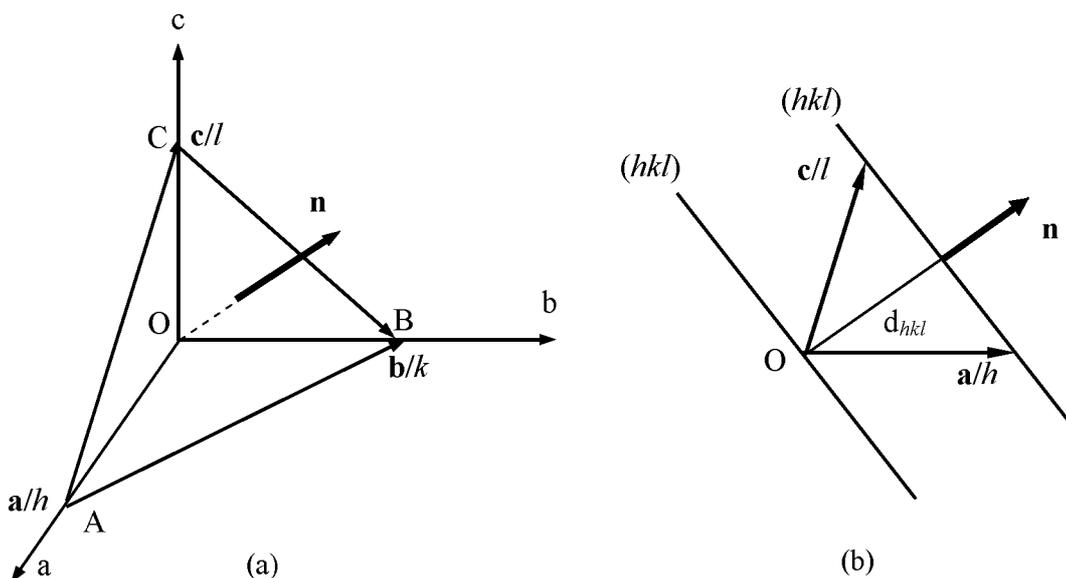


Fig. 1. 6  $(hkl)$  plane in the real space and the plane normal,  $\mathbf{n}$ .

In Fig. 1.6 (b), distance of the  $(hkl)$  plane from the origin  $O$  is  $d_{hkl}$ . Using Eq. (1.7), it is possible to calculate:

$$d_{hkl} = \frac{\mathbf{a}}{h} \cdot \mathbf{n} = \frac{\mathbf{a}}{h} \cdot \frac{\mathbf{r}_{hkl}^*}{|\mathbf{r}_{hkl}^*|} = \frac{1}{|\mathbf{r}_{hkl}^*|}$$

Therefore,  $\mathbf{r}_{hkl}^* = \frac{1}{d_{hkl}} \cdot \mathbf{n} \dots\dots\dots(1.8)$

Eq. (1.8) proves that the reciprocal lattice vector is perpendicular to a set of the  $(hkl)$  planes, and its magnitude is equal to the reverse of the interplanar spacing ( $d_{hkl}$ ) of these planes. As a result of these relations, each reciprocal lattice point represents the corresponding set of  $(hkl)$  planes in the real space.

### 1.5 The Ewald Sphere Construction

In the Bragg's reflection as shown in Fig. 1.7, we consider unit vectors  $\mathbf{S}_0$  and  $\mathbf{S}$  along the incident and scattering directions, respectively. Then the vector,  $\mathbf{S} - \mathbf{S}_0$ , has the direction

perpendicular to the  $(hkl)$  plane. Combining the value of  $\mathbf{S} - \mathbf{S}_o = 2 \sin\theta \cdot \mathbf{n}$  with Bragg's equation (1.3), we can write:

$$\mathbf{S} - \mathbf{S}_o = \frac{\lambda}{d_{hkl}} \cdot \mathbf{n}$$

or, 
$$\frac{\mathbf{S}}{\lambda} - \frac{\mathbf{S}_o}{\lambda} = \frac{1}{d_{hkl}} \cdot \mathbf{n} \dots\dots\dots (1.9)$$

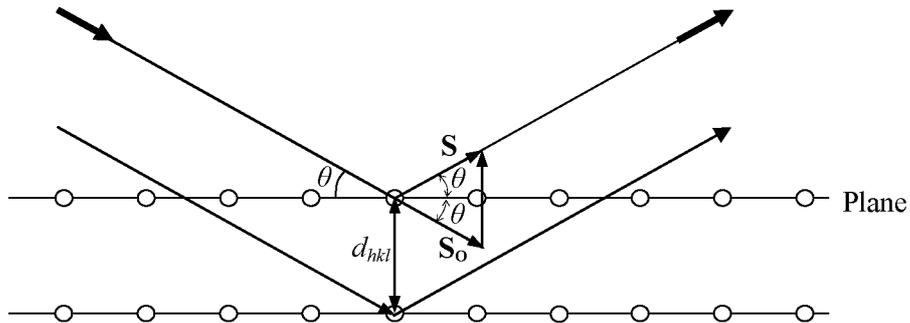


Fig. 1.7 Schematic representation of incident and scattering directions, by unit vectors.

Again, combining Eqs. (1.8) and (1.9), we have:

$$\frac{\mathbf{S}}{\lambda} - \frac{\mathbf{S}_o}{\lambda} = \mathbf{r}_{hkl}^* \dots\dots\dots (1.10)$$

This is the Bragg's condition in the reciprocal space. The condition of constructive interference is satisfied when the vector  $(\mathbf{S}/\lambda - \mathbf{S}_o/\lambda)$  touches a reciprocal lattice point.

The above diffraction condition can be understood by the geometrical construction of Ewald sphere, also known as a sphere of reflection [3]. In the real space, X-rays of wavelength  $\lambda$  are diffracted from  $(\bar{1}20)$  planes of a crystal as shown in Fig.1.8(a). A corresponding representation is illustrated in Fig.1.8(b) in the reciprocal space. The Ewald sphere has a radius  $1/\lambda$ , passing through the origin of reciprocal lattice,  $O^*$ . In this case, the vector  $CO^*$  coincides to  $\mathbf{S}_o/\lambda$ . The vector  $(\mathbf{S}/\lambda - \mathbf{S}_o/\lambda)$  is a chord extending from  $O^*$  to a point on the sphere. Equation (1.10) is satisfied when the reciprocal lattice vector  $\mathbf{r}_{\bar{1}20}^*$  is on the sphere. Generally, the Bragg's condition is satisfied when any reciprocal lattice is on the Ewald sphere.

The Ewald sphere has proved to be a valuable tool for interpreting geometrical relationships between the crystal structure and the corresponding X-ray pattern. Using Eq.(1.10) and Fig.1.8, we know that *the reciprocal lattices, locating on the Ewald sphere, will appear on the X-ray diffraction pattern.*

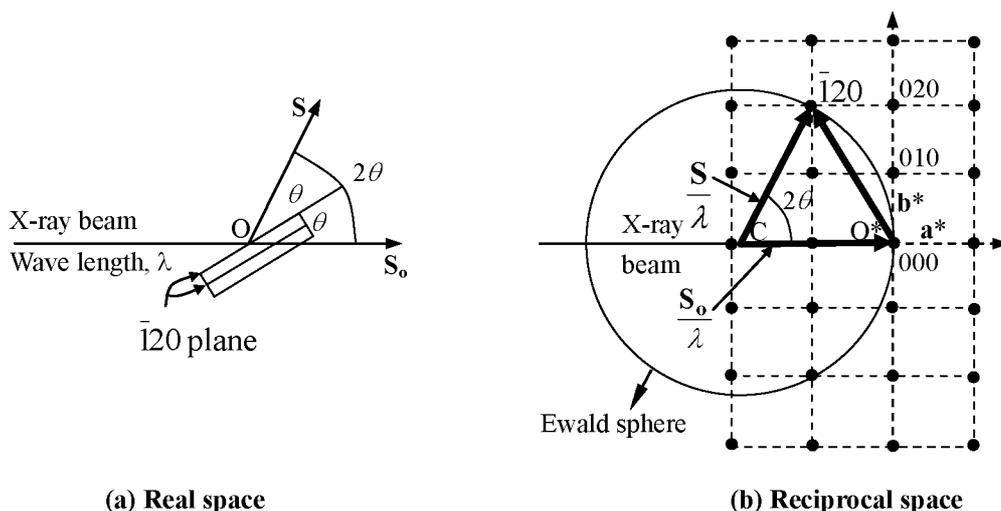


Fig. 1.8. (a) Diffraction condition in the real space, and (b) illustration of Ewald sphere construction in the reciprocal space.

## 1.6 Polymer Structure

Polymeric materials are soft solids, defined by the architecture of long chain molecules. Linear polymers have long chains made of repeating units, where monomers are connected by covalent bonds. The length of the polymer chain is distributed depending on the polymerization. Due to the complicated conformation, polymers reveal various morphologies from amorphous to ordered states. By drawing and/or annealing treatments, the polymers exhibit regular structure and show three-dimensional periodic arrangement at room temperature.

In the polymer morphology, structure units can be classified by the ordering magnitudes: As the first order structure, the monomer unit has several  $\text{\AA}$ . The second ordering appears in the chain conformation such as helix and tacticity in  $\sim 10 \text{\AA}$ . Crystalline lamellae appear as the third order having a scale of  $\sim 100 \text{\AA}$ . As the higher order structures, polymer develops to fibrils ( $\sim 1000 \text{\AA}$ ) and spherulites ( $\sim 10000 \text{\AA} = 1 \mu\text{m}$ ) [4, 5].

Table 1.2. Examples of crystalline structures of some linear polymers.

| Name of polymers                        | Crystal structure | Lattice parameters (Å)  |     |
|---|-------------------|---|-----|
| Polyethylene (PE)                       | Orthorhombic      | $a = 7.37, b = 4.94 \text{ \& } c = 2.55$   | [6] |
| Polypropylene- $\alpha$ ( $\alpha$ -PP) | Monoclinic        | $a = 6.65, b = 20.96 \text{ \& } c = 6.50, \beta = 99.3^\circ$  | [6] |
| Polypropylene- $\beta$ ( $\beta$ -PP)   | Hexagonal         | $a = b = 19.08 \text{ \& } c = 6.49$  | [7] |
| Poly(ethylene terephthalate)<br>(PET)   | Triclinic         | $a = 4.56, b = 5.94 \text{ \& } c = 10.75,$<br>$\alpha = 98.5^\circ \beta = 118^\circ \gamma = 112^\circ$ | [6] |
| Polyoxymethylene (POM)                  | Hexagonal         | $a = b = 4.45, \text{ \& } c = 17.3$  | [6] |

We have extensively studied the morphology and crystallization of some linear polymers, which, in general, exhibit crystalline  $c$ -axis parallel to the chain molecule. Table 1.2 indicates information about the crystal structures of some linear polymers investigated. The detailed discussion will be the main objectives of this book. Lattices of polymer molecules are characterized by a ‘repeat distance’ and a ‘repeat unit’. In most cases, the repeat distance is considered to be nearly equivalent to the length of  $c$ -axis of the unit cell. Due to the limit of the wavelength, X-ray diffraction method is effective to measure the order of several Å to 1000 Å. The larger ordering is studied by electron microscopy, optical microscopy, and light scattering etc.

For detailed presentation of the crystalline lattice and reciprocal lattice, readers may consult the text book of C. Kittel [8].

## References

1. A. Bravais, *J. Ec. Polytech. (Paris)* **19**, 1 (1850)
2. W. Friedrich, P. Knipping, and M. v Laue, *Ann. Physik*, **41**, 971 (1912)
3. P. P. Ewald, *Phys. Z.*, **465** (1913); *Ann. Phys. (Leipzig)* **54**, 519 and 577 (1917)
4. P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, New York (1953)
5. F. W. Billmeyer, Jr., *Text Book of Polymer Science*, 2<sup>nd</sup> ed., pp. 141-154, Wiley Interscience, New York (1971)
6. P. H. Geil, *Polymer Single Crystals*, Interscience Publishers, New York (1963)
7. R. J. Samuels and R. Y. Yee, *J. Polym. Sci (A-2)*, **10**, 385 (1972)
8. C. Kittel, *Introduction to Solid State Physics* (7<sup>th</sup> Ed.) John Wiley & Sons, Inc., New York, (1996)