

RADIAL DISTRIBUTION FUNCTION OF cis-1,4-POLYBUTADIENE BY ELECTRON DIFFRACTION

ZHOU Enle (周恩来)*, KAN Xianglan (阚香兰) and ZHAO Xiaoguang (赵晓光)

(Changchun Institute of Applied Chemistry, Academia Sinica, Changchun)

ABSTRACT

The interatomic distance function of rareearth catalyzed cis-1,4-polybutadiene was studied by radial distribution function (RDF) derived from electron diffraction. Two intramolecular peaks and three intermolecular peaks have been found on the RDF. The appearance of such a number of intermolecular maxima on the RDF can be explained by the local parallel packing of long molecular chains of the amorphous polymers.

INTRODUCTION

The chain conformation of amorphous polymers has been considered by Flory^[1, 2] as a random coil. The coil gives such an unperturbed dimension in bulk as it does in a θ -solvent. But Kargin^[3], Geil^[4] and Yeh^[5], based on their electron microscopy observations, considered that local order exists in amorphous polymers. Recently small-angle neutron-scattering studies on polymer matrices containing small percentages of their deuterated analogues^[6] showed that tagged molecular chains of an amorphous polymer possessed the same radii of gyration in bulk as in solution, in favor of the random coil model. Ovchinnikov and co-workers^[7-9, 17], by using the radial distribution function (RDF) of X-ray and electron diffractions, studied the distribution of interatomic distances, coordination numbers of adjacent atoms and the average interatomic distances of molten polyethylene and natural rubber. They showed the presence of a more or less local lateral parallel packing of molecular chains, analogous to the segment arrangement in its crystal.

The domain structure of cis-1,4-polybutadiene (cis-1,4-PB) has already been reported in detail^[12]. This paper gives the interatomic distances and the number of atoms at any arbitrary distances from a reference atom, based upon the RDF curve Fourier-transformed from an experimental electron scattering intensity curve of cis-1,4-PB. Two intramolecular peaks and three broad intermolecular peaks on the RDF curve were obtained. The appearance of such a number of intermolecular peaks indicates the existence of local order in the amorphous cis-1,4-PB.

THE PRINCIPLE OF RADIAL DISTRIBUTION FUNCTION CALCULATION

The RDF function can be obtained from electron diffraction intensity data by means

* Formerly CHOU Enlo.

Received December 5, 1982

of Fourier transformation^[13]. The Fourier analysis of the experimental intensity curve is based on the equation

$$4\pi r^2 \rho_{(r)} - 4\pi r^2 \rho_0 = \frac{2r}{\pi} \int_0^\infty i(s) \sin(sr) e^{-B\left(\frac{\sin\theta}{\lambda}\right)^2} ds \quad (1)$$

where r is the radial distance from an arbitrary reference atom. $4\pi r^2 \rho_{(r)} dr$ is the average number of atom between r and $r+dr$ from the reference atom. ρ_0 is the average density of the sample in atoms per unit volume. $s=4\pi\sin\theta/\lambda$, θ is the scattering angle, λ the wavelength of the electron beam, and $i(s)$ a structure-sensitive function obtained from the experimental intensity curve I_θ . $e^{-B\left(\frac{\sin\theta}{\lambda}\right)^2}$ is damping factor.

It is noted that the RDF can be derived from $i(s)$ by the Fourier transform (1). The average intensity of scattering $I_c(s)$ equals the experimental intensity I_θ when $s=s_\infty$. It is equal to the sum of scattering intensities of each atom in the sample.

$$i(s) = \frac{1}{j} \left(\frac{I_\theta(s) - I_c(s)}{\sum_i (x_i f_i)^2} \right) = \frac{1}{j} i_1(s) \quad (2)$$

where $\frac{1}{j}$ is the normalization factor; $f_i(s)$ is the electronic elastic scattering factor for the i th atom; x_i is the ratio of number for i th atom.

Both experiments and theoretical calculations show that $i(s)$ satisfies the following equation:

$$\int_0^\infty i(s) ds = 0 \quad (3)$$

thus we can obtain $I_c(s)/f^2(s)$ by graphical analysis:

$$\int_{s_1}^{s_2} \frac{I_\theta(s)}{f^2(s)} ds = \int_{s_1}^{s_2} \frac{I_c(s)}{f^2(s)} ds \quad (4)$$

where

$$f^2(s) = \sum_i (x_i f_i)^2$$

The normalization factor $\frac{1}{j}$ is unknown. It depends on the energy of electron, specimen thickness and other parameters of the instrument. The background may be obtained by many ways, for example, the background obtained from crystalline specimens of the same substance was used to estimate the background for the amorphous material. Nabitovichis^[14] method is used in the present calculation. j can be determined by experimental intensity. Due to the fact that both the elastic scattering intensity and its background are always positive, we can obtain the values of upper and lower limits of j :

$$\left(\frac{I_c(s)}{f^2(s)} - \frac{I_\theta(s)}{f^2(s)} \right)_{\max} < j < \left(\frac{I_c(s)}{f^2(s)} \right)_{\min}$$

In fact we use their average value:

$$j_{\text{aver}} = \frac{1}{2} \left[\left(\frac{I_c(s)}{f^2(s)} - \frac{I_\theta(s)}{f^2(s)} \right)_{\max} + \left(\frac{I_c(s)}{f^2(s)} \right)_{\min} \right] \quad (5)$$

The inelastic scattering background can be subtracted by using j value. Substituting $i_1(s)$ and j into Eq. (1) we obtain

$$4\pi r^2 \rho_{(r)} - 4\pi r^2 \rho_0 = \frac{2r}{\pi j} \int_{s_1}^{s_2} i_1(s) \sin(sr) e^{-B\left(\frac{s}{4\pi}\right)^2} ds \quad (6)$$

The interatomic distance distribution can be calculated by electron computer using Eq. (6).

EXPERIMENTAL

1. Sample

cis-1,4-polybutadiene polymerized by lanthanide catalyst (Ln-PB) was used in this study. The cis-content was 99.8% and the intrinsic viscosity $[\eta]=3.14$ dl/g (toluene, 25°C).

cis-1,4-polybutadiene synthesized by uranium catalyst (U-PB from Italy) possessed a cis-content of $\sim 100\%$ and $[\eta]=3.64$ dl/g.

2. Specimen preparation for electron diffraction

Films were prepared by casting 0.5% toluene solution of the polymer onto a distilled water surface. The thickness of film was about 400 Å. A 200 Å gold film was used to obtain the characteristic curves of the emulsion of the photographic plate.

3. Recording the electron diffraction pattern

The electron diffraction patterns were recorded under exactly the same conditions on photographic plates in a H-500 electron microscope. The distance between the specimen and the plate $L\lambda$, the camera constant, was determined by a gold film. The exposure time for each sample was 0.5, 1, 2, 4, 8, 16 and 32 seconds respectively.

RESULTS

The darkness of the electron diffraction pattern of the gold film was measured on a JENA spectrometer. The darkness curves of electron diffraction graphs for the gold film for different exposure times are shown in Fig. 1. The characteristic curve of emulsion of the photographic plate thus obtained is shown in Fig. 2.

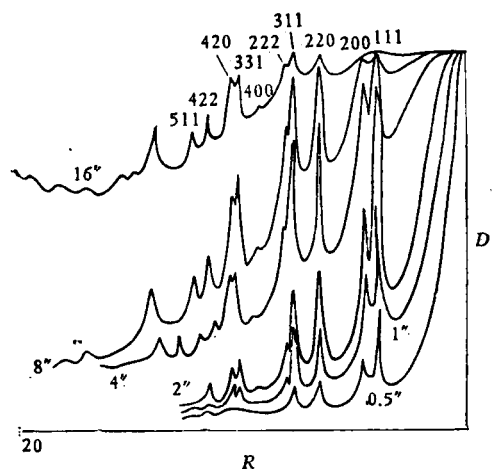


Fig. 1 Darkness curves of electron diffraction graphs of gold film for different exposure time

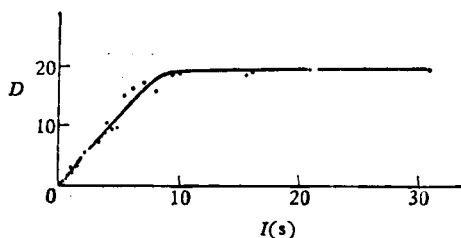


Fig. 2 Characteristic curve of emulsion for photographic plate

Darkness curves of electron diffraction graphs of Ln-PB and U-PB for different times are shown in Fig. 3 and Fig. 4.

The experimental intensity curves of electron diffraction from Ln-PB and U-PB at room temperature are given in Fig. 5.

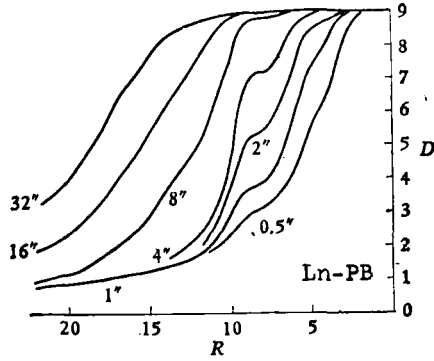


Fig. 3 Darkness curves of electron diffraction graphs of Ln-PB for different exposure time

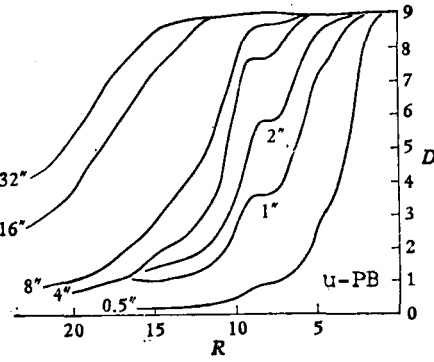


Fig. 4 Darkness curves of electron diffraction graphs of U-PB for different exposure time

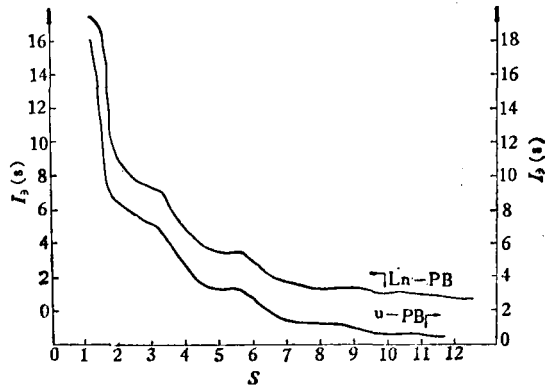


Fig. 5 Experimental intensity curves of electron diffraction from *cis*-1,4-PB at room temperature

Scattering factor $f^2(s)$ was calculated by equation $f^2(s) = \sum_i (x_i f_i)^2$ with the f_O and f_H from the literature [15]. Since C_4H_6 is the chemical structural unit of cis-1,4-PB, $X_H=60$, $X_O=40$ were assumed.

The function $\frac{I_\theta(s)}{f^2(s)}$ and $\frac{I_c(s)}{f^2(s)}$ versus s for Ln-PB and U-PB are shown in Fig. 6. The function $\frac{I_c(s)}{f^2(s)}$ was calculated by a least-squares curve-fitting program according to Eq. (4). $\frac{I_c(s)}{f^2(s)}$ is a smooth curve.

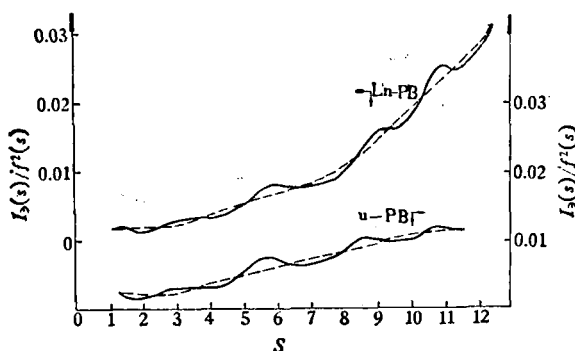


Fig. 6 Function $\frac{I_\theta(s)}{f^2(s)}$ and $\frac{I_c(s)}{f^2(s)}$ versus s for Ln-PB and U-PB

The structure sensitive function $i_1(s)$ was obtained by Eq. (2). The curves $i_1(s)$ versus s are shown in Fig. 7. The factor of normalization $\frac{1}{j}$ was obtained by Eq. (5).

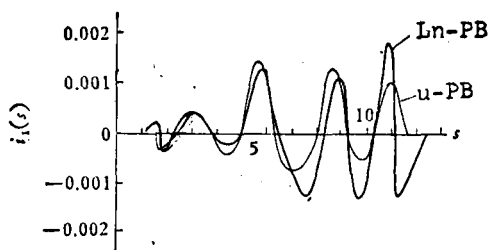


Fig. 7 Structure sensitive function $i_1(s)$ versus s

The Fourier transformation was carried out according to Eq. (6). The step Δs was set equal to 0.02, $B=4$ Å. The computation was done by a Model 130 computer using BASIC language. The radial density curve $4\pi r^2 \rho(r)$ obtained is given in Fig. 8.

DISCUSSION

Four peaks with Bragg spacing $d=0.68$, 1.05, 2.03 and 4.05 Å are present in the experimental intensity curve of electron diffraction for Ln-PB and U-PB (Fig. 5). The RDF (Fig. 8) corresponding to the experimental intensity curve of electron diffraction gives 5

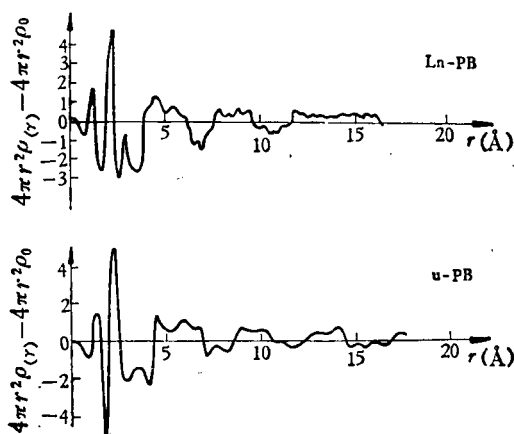


Fig. 8 Radial distribution function for Ln-PB and U-PB

peaks. On the RDF curve there are two peaks at r -values of 1.5 and 2.5 Å. These peaks correspond to the intramolecular distances between carbon atoms (C_1-C_2 and C_1-C_3) along the polymer chain. In the range of $r > 4$ Å, there appear to be 3 broad peaks. They are in the range of 4–6 Å, 8.5–9.5 Å and 12–16 Å respectively, corresponding to the intermolecular distances. Those peaks are similar to the results of Ovchinnikov for polybutadiene (the samples studied by them contained 30% *cis*-1,4-PB; 63.5% *trans*-1,4-PB and 6.5% 1,2 links)^[17] (Fig. 9) at 20°C. Intermolecular peaks given by Ovchinnikov are in the range from 3.3 to 6.1 Å and from 8.6 to 10.3 Å. And they have found that the mean intermolecular distance (which was determined from the RDF curves for the amorphous PB) was equal to the mean intermolecular distance, which was calculated on the base of elementary cell of PB (its unit cell is monoclinic with cell constants of $a=4.60$ Å, $b=9.50$ Å, $c=8.60$ Å and $\beta=109^\circ$). They pointed out that there was a small difference between the densities of amorphous PB and of the crystalline one. The peaks we observed occur in the range of radius of less than 15 Å. So the least size of ordered regions is about 30 Å. This size corresponds to the size of nodule observed by electron microscope.

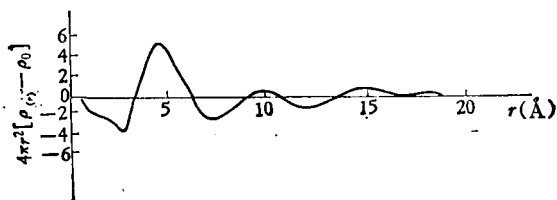


Fig. 9 Radial distribution function for polybutadiene at room temperature^[17]

The above experimental observations show that although the long range three dimensionally ordered packing of atoms in the *cis*-1,4-PB at room temperature is absent, the short range three dimensional order such as distorted monoclinic lattice still maintains. Due to the long chains and high viscosity of polymer systems, the macromolecules are not able to move even at a temperature above its melting point. Therefore the thermodynamic equilibrium, random coil, is not reached and the local order between the molecular chains is

maintained, which leads to a series of structures with various degrees of parallel packing. This explains the fact that cis-1,4-PB can completely crystallize in a few minutes at low temperature and there is memory effect in the recrystallization of polymers. This is the result of certain local order between the molecules in the elastic state. In order to eliminate the local order between the molecules during processing and get homogeneous product with good properties, it is necessary to keep the processing temperature much higher than its melting point. On the other hand the local order is so incomplete that the X-ray and electron diffraction patterns typical of crystalline structures are not available, the intermolecular peaks on the RDF are very wide and small, indicating that the degree of ordering is very low.

In summary, the interatomic distance distribution of cis-1,4-PB can be explained by a model that there exist a series of structures with various degrees of parallel packing. The mechanical and thermal properties of cis-1,4-PB also can be explained by this model.

REFERENCES

- [1] Flory, P. J., *J. Macromol. Sci., Physics*, **1976**, B12, 1.
- [2] Flory, P. J., "Principles of Polymer Chemistry", Cornell University Press, **1953**.
- [3] Kargin, V. A., Kitaigorodsky, A. I., Slonimsky, G. L., *Colloid. J. USSR* (English Translation), **1957**, 19, 141.
- [4] Geil, P. H., "Polymeric Materials", American Society for Metals, Park, Ohio, **1963**, p. 119.
- [5] Yeh, G. S. Y., *J. Macromol. Sci., Physics*, **1972**, B6, 451.
- [6] Schmertz, W., Springer, T., Schelten, J., Ibel, K., *J. Appl. Cryst.*, **1974**, 7(2), 96.
- [7] Овчинников, Ю. К., Маркова, Г. С., Карчин, В. А., *ДАН СССР*, **1966**, 171, 1368.
- [8] Овчинников, Ю. К., Маркова, Г. С., *Высокомолек. Соед.*, **1967**, A9, 449.
- [9] Овчинников, Ю. К., Маркова, Г. С., Каргин, В. А., *Высокомолек. Соед.*, **1968**, A2, 329.
- [10] Voigt-Martin, Mighoff, F. C., *J. Appl. Phys.*, **1975**, 46, 1165.
- [11] Wang, C. S., Yeh, G. S. Y., *J. Macromol. Sci., Physics*, **1978**, B15, 107.
- [12] 周恩乐、徐白玲、贾连达, 高分子通讯, **1981**, (1), 27.
- [13] Вахитович, В. К., *Кристаллография*, **1957**, 2, 29.
- [14] Набитович, И. Д., Стецев, Я. И. и Волощук, Я. В., *Кристаллография*, **1967**, 12, 584.
- [15] Hirsch, P. B., Howie, A., Nicholson, R. B., Pashley, D. W., Whelan, M. J., "Electron Microscopy of Thin Crystals", Butterworths, London, **1971**.
- [16] 周恩乐、徐白玲, 高分子通讯, **1982**, (3), 198.
- [17] Markova, G. S., Ovchinnikov, Ju. K., Boknyan, E. B., *J. Polymer Sci.*, **1973**, C42, 671.
- [18] 季达依哥罗茨基著, 龚尧圭等译, "X 射线结构分析" 科学出版社, **1953**.