

THE INFLUENCE OF HEAT TREATMENT ON STRUCTURES OF THE AGGREGATED STATE OF POLYAMIDE-1010*

ZHANG Hongfang (张宏放) YANG Baoquan (杨宝泉)

and MO Zhishen (莫志深)

(Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022)

ABSTRACT

The structural parameters of the aggregated state of polyamide (PA)-1010 annealed at various temperatures were computed by means of the desmearing intensity from Small Angle X-ray Scattering (SAXS) measurements and by using the concept of the distance distribution function. The results indicated that the structural parameters of the aggregated state were strongly dependent upon heat treatment conditions and the maximum values of the structural parameters were obtained for the samples annealed at $T = 175^{\circ}\text{C}$. The particle size Z annealed at different temperature was ranged between 8.1–12.8nm, and the values of the distance distribution function $P_{\max}(Z)$ were obtained when $Z = 4.0\text{--}6.8\text{nm}$. Using one dimension electron density correlation function (1D EDCF) method long period (L) and thickness of the lamellar (d_0) were estimated and were found to increase with the increase of the degree of crystallinity.

INTRODUCTION

As an important high performance engineering plastics, polyamide (PA)-1010 was characterized by its low moisture absorption and high dimensional stability. The studies on the crystal structure, thermodynamic properties and irradiation effects of PA-1010 have been reported^[1–3]. In the present paper, small angle X-ray scattering (SAXS) technique was applied to calculate structural parameters of the aggregated state of PA-1010 samples. SAXS measurement can be used to characterize the size and shape of domain in the multicomponent polymer^[4] and to estimate the interfacial thickness^[5], phase separation^[6]. Kube has performed error analysis of a smeared SAXS curve^[7]. The particle size distribution obtained by using different calculating methods from SAXS was discussed^[8]. In order to extend the study on SAXS technique, our work was focused on some structural parameters of the aggregated state of PA-1010 at various annealing temperatures.

*The project was supported by the National Key Projects for Fundamental Research "Macromolecular Condensed State", The State Science and Technology Commission of China.

Received May 8, 1995

EXPERIMENTAL

1. Materials and samples

PA-1010 $-\text{[CO(CH}_2\text{)}_8\text{CO-NH(CH}_2\text{)}_{10}\text{NH]}_n$ used in this work was a commercial product of Jilin Union Chemical Work, Jilin, China. The viscosity-average molecular weight $\overline{M}_\eta$ determined in m-cresol solution was 1.34×10^4 . Its melting point was ca. 210°C . Powdered PA-1010 samples were vacuum dried at 90°C for 2 days, and then fully melted in a molding press at about $T = 220^\circ\text{C}$ for 30min and pressed into a disc of 0.1cm thickness at $T = 195^\circ\text{C}$, 185°C , 175° , 165°C and 80°C , respectively under a pressure of 9.8MPa for 1h. These samples were gradually cooled down to room temperature.

2. SAXS measurement

Collection of SAXS data at room temperature was carried out by means of a Philips PW-1700 X-ray diffractometer equipped with a Kratky small angle X-ray camera, a step scanning device and a scintillation counter. The distance between sample and detector was 20cm. All the measurements were performed with CuK_α radiation source operating at 45kV and 40mA. Monochromatization was achieved by using a graphited crystal.

The exposure time was 2h for all the samples tested. This counting time is long enough to avoid the influence of noise on the scattering intensity, so that during the process of data collection count error was less than a 1% for the largest angle. The scattering intensities were corrected for an absorption, background and incident X-ray intensity fluctuations of the samples. Desmeared scattering intensities were obtained by using a procedure developed by Schmidt^[9] on the slit-smeared effects. The resulting curves were converted to absolute scattering intensity with the help of a calibrated Lupolen standard sample^[10].

RESULTS AND DISCUSSION

Fig.1 shows curves of SAXS intensities I vs. scattering angle θ for the samples at different annealing temperatures. As shown in Fig.1, scattering intensities I increase with increasing the degree of crystallinity $W_{C,X}$ (see Table 1). On the basis of Debye-Bueche theory^[11], if the system is assumed that a random heterogeneous medium consists of the particles with the same shape but different size and that no interference or multiple scattering effects exist among particles. Scattering intensity can be described as follows:

$$I(h) = 4\pi \int_0^\infty \gamma(Z) Z^2 \frac{\sin(hZ)}{hZ} dZ \quad (1)$$

where $\gamma(Z)$ is a correlation function, the reduced scattering angle h is defined by $h = 4\pi \sin \theta / \lambda$, λ the wavelength of the radiation. θ is the angle between primary beam and scattered radiation. Z is the characteristic dimension of the particle. Eq.(1) connected directly with the distance distribution function $P(Z)$, so that Eq.(1) can now be expressed by^[12]:

$$I(h) = 4\pi \int_0^\infty P(Z) \frac{\sin(hZ)}{hZ} dZ \quad (2)$$

where $P(Z) = \gamma(Z)Z^2$. In order to compute the distance distribution function $P(Z)$, a conventional inverse Fourier transformation of Eq.(2) can be carried out:

$$P(Z) = \frac{1}{2\pi^2} \int_0^\infty I(h)(hZ) \sin(hZ) dh \quad (3)$$

$I(h)$ in Eq.(3) is a slit desmearing intensity. With the help of $P(Z)$, an approximate value for the intensity at zero angle $I(0)$:

$$I(0) = 4\pi \int_0^{D_{\max}} P(Z) dZ \quad (4)$$

where $D_{\max}$ is a maximum particle size, which can be obtained from the curve of $P(Z)$ vs. Z at $P(Z) = 0$, and a radius of gyration of the whole particle R_g^2 :

$$R_g^2 = \frac{\int_0^{D_{\max}} P(Z) Z^2 dZ}{2 \int_0^{D_{\max}} P(Z) dZ} \quad (5)$$

Baur pointed out that the average radius R_i is associated with certain ratios of various moments of the dimensional distribution, if the particles with homogeneous spheres are assumed^[13]. Thus, for each structural parameter, which are the correlation length l_c , the correlation volume and the radius of gyration of whole particle, an average radius R_i ($i = l_c, V, G$) of the spheres can be also obtained as follows:

$$R_{Lc} = \frac{2}{3} \langle l_c \rangle, \quad R_V^3 = \left(\frac{3}{4\pi} \right) \langle V \rangle, \quad R_G^2 = \frac{5}{3} \langle R_g \rangle^2 \quad (6)$$

Also, by means of the slit desmearing intensity $I(h)$, invariant Q , correlation length l_c and specific surface O_s are revealed as follows:

$$l_c = \frac{\pi \int_0^\infty I(h) h dh}{Q} \quad (7)$$

$$O_s = \frac{\pi \lim_{h \rightarrow \infty} [I(h) h^4]}{Q} \quad (8)$$

The invariant Q in Eqs.(7) and (8) can be also determined by 1D EDCF method. The method is based on the linear model, which assumed that the dimensions of

the stack parallel and normal to the lamellar surfaces are large compared to the interlamellar distance. The correlation function $K(Z)$ is related to electron density variation along the lamellar normal and is computed by^[14]

$$K(Z) = \frac{1}{\pi} \int_0^\infty I(h) h^2 \cos(hZ) dh \quad (9)$$

On the basis of the curve of $K(Z)$ vs. Z , one can estimate the long period L , the thickness of lamellar d_0 , invariant Q .

By the aid of Eq.(3), $P(Z)$ curve was computed and drawn in Fig.2.

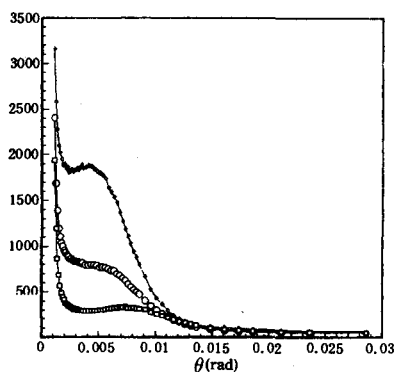


Fig.1 The SAXS curves of I vs. θ at different annealing temperatures

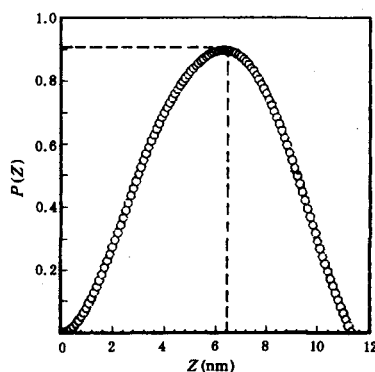


Fig. 2 The curve of distance distribution function $P(Z)$ vs. characteristic size Z for annealing temperature at 185°C

As shown in Fig.2, $P(Z)$ curve is a normal distribution (or bell-type). Values of $P(Z)$ computed by Eq.(3) with various annealing temperature were listed in Table 1, values of $P_{\max}(Z)$ and the particle size $Z_{\max}$ (at $P(Z) = 0$) can be determined (Fig.2). As indicated in Table 1, probability maximum value of $P_{\max}(Z)$ was obtained nearby $T = 175^\circ\text{C}$. Comparing $Z_{\max}$ and $P_{\max}(Z)$ with $W_{C,X}$, one can find that the higher degree of the crystallinity of the samples, the greater is the values of $P_{\max}(Z)$ and $Z_{\max}$. This suggests that the regularity of the molecular chains of PA-1010 is obviously improved by annealing, this necessarily led to the increase of the degree of crystallinity and the electron density difference $\Delta\rho$ of the system. In addition, the scattering intensity $I(h)$ is directly proportional to the square of $\Delta\rho$, and according to Eq.(3) $P(Z)$ is proportional to $I(h)$, therefore, the values of distance distribution function $P_{\max}(Z)$ and the particle size Z increase with the increase of the degree of crystallinity of the system.

Other structural parameters of the aggregated state for PA-1010, such as $I(0)$, R_i^2 , I_C and O_S , were estimated by using Eqs.(4)–(8) and were tabulated in Table 1. With the help of above mentioned discussion, the following conclusions can be obtained in which $I(0)$, Q and R_i ($i = g, G, l_C, V$) increase with the in-

crease of the degree of crystallinity. It is obvious that high crystalline samples were obtained by annealing at about $T = 175^{\circ}\text{C}$, wherein a regular arrangement of molecular chains were favored by PA-1010. The specific surfaces O_s as a function on a temperature which is defined as the ratio of the area of the phase interface to the volume occupied by the disperse phase. From Table 1 one can find that the sample with higher crystallinity possessed smaller specific surface O_s , this result fitted in with the discussion above on the particle sizes Z , i.e. greater Z which occupied larger volume, so that the number of the grains in unit volume decreased.

Table 1 Some structural parameters for PA-1010 samples at various annealing temperatures

Temp.($^{\circ}\text{C}$)	195	185	175	165	80
$Q \times 10^4 (\text{mol} \cdot \text{e}/\text{cm}^3)^2$	1.26	1.64	2.28	1.75	0.80
$I(0)^*$	5.129	8.332	12.598	8.961	1.323
$P_{\max}(Z) \times 10^2$	0.660	0.957	1.544	1.116	0.225
$Z_{\max} (\text{nm})$	10.7	11.8	12.8	11.0	8.1
$O_s (\text{nm}^{-1})$	0.204	0.199	0.142	0.153	0.345
$l_c (\text{nm})$	10.05	11.01	10.33	9.99	8.54
$L (\text{nm})$	17.3	17.6	18.0	18.0	12.4
$d_0 (\text{nm})$	2.92	3.12	4.00	3.70	1.38
$R_g (\text{nm})$	4.36	4.86	4.74	4.64	3.24
$R_G (\text{nm})$	5.62	6.27	6.12	5.99	4.18
$R_{lc} (\text{nm})$	6.70	7.34	6.89	6.66	5.92
$R_v (\text{nm})$	6.22	6.19	6.35	6.20	4.25
$W_{C,X}(\%)^{**}$	40.3	42.5	47.2	43.6	15.0

* Absolute intensity ** WAXD results

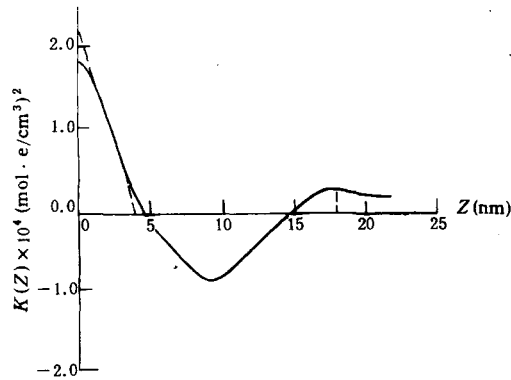


Fig.3 The curve of experimental correlation function $K(Z)$ obtained for PA-1010 sample with annealing temperature at 175°C

On the basis of the 1D EDCF method, the long period L and the thickness of the lamellar d_0 (which is a point of intersection of the straight section in the self-correlation range with lateral coordinate Z) for PA-1010 were estimated and described in Fig.3 and Table 1.

Table 1 indicated that long period L and the thickness of the lamellar d_0 were

closely related with annealing temperature. The result obtained by differential scanning calorimeter (DSC) indicated that the sample of PA-1010 has two melting peaks at $T_{m1} = 190^{\circ}\text{C}$ and $T_{m2} = 210^{\circ}\text{C}$ respectively^[15]. On the basis of this result, it is known that the higher the annealing temperature, the stronger is the ability of moving and folding of molecular chains of PA-1010, however, at very high annealing temperature, for example at $T > 185^{\circ}\text{C}$, movement of the molecular chains of PA-1010 is so vigorous that the stack of the molecular chains is unable to form a stable microcrystal structure and part of the molecular chains may appear as melting state. On the contrary, at low annealing temperature the moving energy of chain segment obtained was too low, which is detrimental to the formation of regular arrangement of the molecular chains. It can be concluded that higher crystallinity and more perfect crystal are formed for PA-1010 by annealing at $T = 175^{\circ}\text{C}$. The values of L and d_0 increase with the increase of the crystallinity. It was also noted that d_0 changed significantly, but L changed very slightly by annealing. It implied that the regions of the amorphous part of PA-1010 was reduced in the regions of the crystal phase by annealing. On the basis of the above discussion, the thermal history has significantly effects on the structures of aggregated state of PA-1010.

Keywords:

Polyamide-1010; SAXS; Heat treatment; Structure of aggregated state

REFERENCES

- [1] Mo, Z.S.; Meng, Q.B.; Feng, J.H., et al., *Polymer International*, **1993**, 32: 53.
- [2] Feng, J.H.; Zhang, L.H. and Chen, D.L., *Radiat. Phys. Chem.*, **1991**, 38: 105.
- [3] Zhang, L.H.; Yu, L. and Zhang, H.F., *Chinese J. Appl. Chem.*, **1992**, 9(5), 21.
- [4] Sperling, L.H., *Polym. Mater. Sci. Eng.*, **1988**, 59: 150.
- [5] Perrin, P. and Prud'homme, R.E., *Macromolecules*, **1994**, 27: 1852.
- [6] Meier, H. and Strobl, G.R., *Macromolecules*, **1987**, 20: 649.
- [7] Kube, O.; Springer, J., *J. Appl. Cryst.*, **1985**, 18: 308.
- [8] Walter, G.; Kranold, R. and Gerber, Th., *J. Appl. Cryst.*, **1985**, 18: 205.
- [9] Schmidt, P.W., *Acta. Cryst.*, **1965**, 19: 938.
- [10] Kratky, O.; Pitz, I. and Schmitz, P.J., *J. Colloid Interface Sci.*, **1966**, 21: 24.
- [11] Debye, P. and Bueche, A., *J. Appl. Phys.*, **1949**, 20: 518.
- [12] Glatter, O. and Kratky, O., "Small Angle X-Ray Scattering" Academic Press, New York, **1982**.
- [13] Baur, R. and Gerold, V., *Acta Metal.*, **1964**, 12, 1448.
- [14] Strobl, G.R.; Schneider, M.J. and Voigt-Martin, I.G., *J. Polym. Sci., Polym. Phys. Ed.*, **1980**, 18: 1361.
- [15] Zhu, C.S.; Wang, J.W. and Yang, G.P., *Acta Polymerica Sinica* (in Chinese), **1993**, 2: 165.