

DETERMINATION OF THE CRYSTALLINITY IN DIFFERENT TYPE POLY (OXYETHYLENE – STYRENE) BLOCK COPOLYMERS BY X – RAY DIFFRACTION METHOD

YAO Ning (姚 宁)

(Hubei Research Institute of Chemistry, Wuhan)

ABSTRACT

By means of the intensity theory of X-ray scattering and the two-phase concept of high polymer, the basic formula of the crystallinity in block copolymers has been proposed after the corrections of atomic, temperature, absorption, Lorentz and polarization factor. Application of this method to different type poly (oxyethylene – styrene) block copolymers and the same type block copolymers with different EO contents indicates that the crystallinity in poly (oxyethylene – styrene) block copolymers increases with the increase of the EO content and decreases in the order: PEO – PS – PEO > PEO – PS > PS – PEO – PS.

INTRODUCTION

The physical and mechanical properties of polymers are profoundly dependent on the degree of crystallinity. Among the measurement techniques used for determining polymer crystallinity, X-ray diffraction methods play a predominant part^[1]. The method of Hermans and Weidinger^[2] proposed for determining the degree of crystallinity in natural and manmade fibers was in general use, as were the integral and correlation methods of Wakelin et al.^[3] for cellulose fibers and others^[4,5]. Ruland's method and being considered again in a more simplified form by Vonk^[6,7] took into account the scattered intensity over a wide zone of reciprocal space and enabled the "apparent crystallinity" to be corrected by a disorder parameter. Johnson et al.^[8-10] tried to redefine the method of calculating the crystallinity in polymer in specifying a disorder parameter. Their method was based on the resolution of normalized diffraction peaks in terms of combined Gaussian – Cauchy profiles for each peak, together with a polynomial background. This is precisely the case when examinations are carried out on specimens in which the orientation of structural elements is a random one. Mo et al.^[11,12] have calculated the crystallinity in syndiotactic 1, 2 – PBD and eight PET fibers using the atomic scattering factors approximation expression and computer. Their method can be used to calculate the crystallinity in the polymer with known crystalline structure.

Up to now, all the X-ray diffraction methods reported in literature^[1-13] for calculating the crystallinity in polymer are based on the following assumptions:

(1) The scattering capability of crystalline is equal to that in amorphous with the same mass.

(2) The intensity of the X-ray scattered from a specimen is approximately equal to the sum of that from the crystalline and amorphous in the specimen.

It is obvious that the two assumptions above are not reasonable to copolymers since the scattering and absorption capability of crystalline and those of amorphous are not the same, due to the difference of individual composition. Thus, the X-ray diffraction method used at present for determining the crystallinity in polymer can only be applied to homopolymer, but not to copolymer.

In the present paper we aimed at to discuss a new X-ray diffraction method for the calculation of the crystallinity in block copolymers based on the intensity theory of X-ray scattering and the two-phase concept of high polymer. And the determination of the crystallinity in different type poly (oxyethylene-styrene) block copolymers was illustrated.

THEORY

The intensity of the X-ray scattered over all angles by a given assemblage of atoms is independent on their state or order or disorder. It follows that if the crystalline and amorphous scattering in the diffraction pattern can be separated from each other, the total scattering is equal to the scattering of crystalline and amorphous^[14]:

$$4\pi \int_0^\infty s^2 I(s) ds = 4\pi \int_0^\infty s^2 I_c(s) ds + 4\pi \int_0^\infty s^2 I_a(s) ds \quad (1)$$

where $s = 2\sin\theta/\lambda$, magnitude of the radical vector in the reciprocal space (2θ = diffraction angle, λ = wavelength expressed in Å); $I(s)$ = intensity of coherent X-ray scattered; $I_c(s)$ = part of the intensity which is concentrated into crystalline peaks; $I_a(s)$ = part of the intensity which is concentrated into amorphous peaks.

In general, the compositions of crystalline and amorphous in block copolymers are not the same. So the total scattering should be equal to the sum of scattering of each component in a specimen. Let M and P be the number of components of crystalline and amorphous in a specimen, respectively, equation (1) may be further developed as follows:

$$4\pi \int_0^\infty s^2 I(s) ds = \sum_{i=1}^M 4\pi \int_0^\infty s_i^2 I_{ci}(s_i) ds_i + \sum_{k=1}^P 4\pi \int_0^\infty s_k^2 I_{ak}(s_k) ds_k \quad (2)$$

Because the crystalline fraction is equal to the ratio of the integrated crystalline scattering to the total scattering, both crystalline and amorphous, the basic formula for the calculation of the crystallinity in block copolymer can be written as:

$$X_c = \frac{\sum_{i=1}^M \int_0^\infty s_i^2 I_{ci}(s_i) ds_i}{\sum_{i=1}^M \int_0^\infty s_i^2 I_{ci}(s_i) ds_i + \sum_{k=1}^P \int_0^\infty s_k^2 I_{ak}(s_k) ds_k} \quad (3)$$

where X_c = weight fraction of the crystalline material in the block copolymer, namely, crystallinity.

A number of experimental fractions modify the ideal intensity $|F^2|$ to yield the intensity that is actually observed, $I(hkl)^{[14]}$:

$$I(hkl) = P \cdot L \cdot j \cdot A \cdot |F^2| \quad (4)$$

where $P = \frac{1}{2} (1 + \cos^2 2\theta)$, polarization factor; $L = \frac{1}{\sin 2\theta \cos \theta}$, Lorentz factor; j = multiplicity factor; A = absorption factor; F = structure factor, which is reduced by a temperature factor of the form $\exp(-2M)$ defined by a single numerical value of the coefficient $M = B (\sin^2 \theta / \lambda^2)$.

In examining the specimen with different crystallinity and taking into account the factors above, it is possible to define a correction coefficient such as the equation

$$C^{-1} = f^2 \cdot \exp\left(-2B \frac{\sin^2 \theta}{\lambda^2}\right) \cdot \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \cdot A \quad (5)$$

where f = the atomic - scattering factor of the total atoms per unit mass of each component of the specimen.

The multiplicity factor j is not included in equation (5) because it does not affect the calculation of the crystallinity in polymer. Under these conditions and changing the integration over the whole of reciprocal space into the summation of integral intensity of each peak, equation (3) becomes,

$$X_c = \frac{\sum_{i=1}^M \sum_{j=1}^N C_{ij} \cdot I_{cij}}{\sum_{i=1}^M \sum_{j=1}^N C_{ij} \cdot I_{cij} + K \cdot \sum_{k=1}^P \sum_{l=1}^Q C_{kl} \cdot I_{akl}} \quad (6)$$

where N = the number of the crystalline peaks of component i ; Q = the number of the amorphous peaks of component k ; K = constant, applied to correcting the reduced intensity resulting from collected diffraction data over the limited angular range.

Equation (6) may therefore be used to the block copolymers that the scattering of crystalline and amorphous in the diffraction pattern can be separated from each other.

EXPERIMENTAL

The samples used for this work were three types of poly (oxyethylene - styrene) block copolymers. The PEO - PS diblock copolymer was synthesized in toluene by α - phenylethyl potassium as initiator. The PS - PEO - PS triblock copolymer was prepared by coupling two moles of the PEO - PS diblock copolymer containing one hydroxyl end group, using toluene diisocyanate as coupling agent. The PEO - PS - PEO triblock copolymer was made by polymerizing styrene in toluene using potassium naphthalene as bifunctional initiator, then copolymerizing with EO. The copolymers were purified by extraction and characterized by GPC, proton NMR, IR, UV, and DSC. All the results indicate that the purified polymers are really block copolymers^[15, 16].

A Rigaku 3015 diffractometer was used employing $\text{CuK}\alpha$ radiation at the following parameters: accelerating voltage, 35kV, anodic current, 25 mA. Diffraction angle

2θ from 10° to 30° at a rate of $0.5^\circ/\text{min}$. The specimen rotation attachment was used to reduce the effect of orientation in the block copolymers.

RESULTS AND DISCUSSION

The crystallographic data and density of homopolyoxyethylene (PEO) and homopolystyrene (PS) are shown in Table 1.

Table 1 Crystallographic data and density of PEO and PS

Homopolymer	Crystal system	Unit cell dimensions				Density (g/cc)	
		a	b (Å)	c	β ($^\circ$)	Crystal	Amorphous
PEO ^[17]	Monoclinic	7.95	13.11	19.39	124.6	1.231	—
PS ^[18]	Rhombic	22.08	22.08	6.63	—	1.112	1.040

Normalized equatorial diffraction traces over the angular range from 10° to 30° of PEO, PS, and PEO-PS block copolymer are given in Figure 1.

The experimental results shown in Figure 1 evidently indicate that PS is fully amorphous with its halo centered at 19.3° and PEO is almost crystalline with its two major peaks at 19.1° and 23.3° . In the diffraction pattern of PEO-PS block copolymer, in addition to the amorphous halo of PS still at 19.3° , this angular range encompasses two strong crystalline peaks with the same angular as PEO and the intensity of the two peaks increases with EO content of PEO-PS block copolymer. This result shows that the intensity of crystalline scattering is the contribution of PEO block and the intensity of amorphous scattering can be regarded as the contribution of PS

block approximately in the diffraction pattern of PEO-PS block copolymer. Thus, the crystalline and amorphous scattering in the diffraction pattern of PEO-PS block copolymer can be resolved as the method of Challa, Hermans and Weidinger^[19].

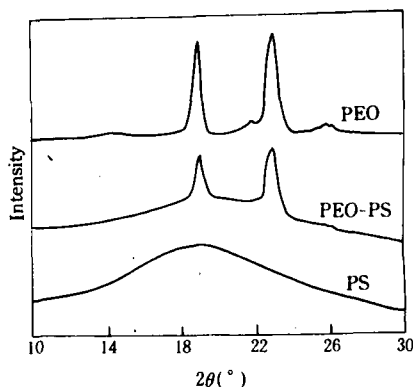


Fig.1 X-ray scattering curves of PEO, PS and PEO-PS block copolymer.

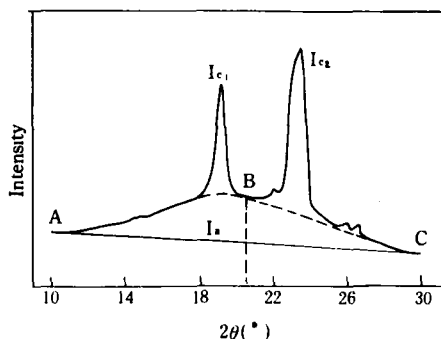


Fig.2 Procedure for cutting off the background scattering and resolution of crystalline and amorphous scattering

The procedure of cutting off the background scattering and resolution of crystalline and amorphous scattering are shown in Figure 2. It consists of the following steps: (a) The angular range of measurement is chosen from 10° to 30° . (b) A straight line is drawn from A to C, separating the intensity components "above" from the intensity components "below". (c) Select an intermediate point B (20.5°) at which the crystalline intensity is assumed to drop to zero (The separation between

the two major crystalline peaks is 4.2° , which is regarded as large enough to justify this assumption). (d) The line of demarcation ABC between the amorphous and crystalline scattering is drawn in so as to be congruent with the profile of the amorphous PS in this region (Figure 1).

The total area above the curve ABC in Figure 2 is now taken to be proportional to the intensity of crystalline scattering, I_{c1} and I_{c2} , and the area between the lines ABC and AC is taken to be proportional to the intensity of amorphous scattering, I_a .

By means of equation (5) the correction coefficient was calculated for the two major crystalline peaks of PEO block and the amorphous halo of PS, taking into account the atomic, temperature, absorption, Lorentz and polarization factors (Table 2). Normalizing the values of correction coefficient C and then substituting it into equation (6), the calculation formula of the degree of crystallinity for poly (oxyethylene-styrene) block copolymers can be written as follows:

$$X_c = \frac{1.45I_{c1} + 2.72I_{c2}}{1.45I_{c1} + 2.72I_{c2} + K \cdot I_a} \times 100\% \quad (7)$$

Table 2 Calculation of the correction coefficient of PEO-PS block copolymers

	Peaks		
	I_{c1}	I_a	I_{c2}
$2\theta (^\circ)$	19.1	19.3	23.3
$2B$	8	10	8
$\exp(-2B \frac{\sin^2 \theta}{\lambda^2})$	0.9115	0.8885	0.8718
$\cdot \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$	69.74	68.25	46.16
f^2	242.0	198.0	204.1
μ_m	6.73	4.28	6.73
$A = \frac{1}{2\mu_m \cdot \rho}$	0.0604	0.1123	0.0604
C	1.45	1.00	2.72
K	—	0.81	—

In order to obtain the value of K , the diffraction data of PEO over the angular from 10° to 90° was collected and the ratio of the intensity of the two major crystalline peaks, I_{c1} and I_{c2} , to the total intensity of all crystalline of PEO over the angular form 10° to 90° was found to be 0.81. Thus, the value of K is 0.81 and equation (7) may then be further developed:

$$X_c = \frac{1.45I_{c1} + 2.72I_{c2}}{1.45I_{c1} + 2.72I_{c2} + 0.81I_a} \times 100\% \quad (8)$$

Using equation (8), the crystallinity in different type poly (oxyethylene-styrene) block copolymers can be calculated. Table 3 lists the degree of crystallinity obtained with equation (8) and the method of Hermans and Weidinger.

Table 3 Measurements of the crystallinity in poly (oxyethylene – styrene) block copolymers

No .	Type	EO%	Degree of crystallinity (%)
1	BAB*	37.1	48.0 (47.2)**
2	BAB	53.9	80.0 (79.2)
3	AB	33.5	9.4 (9.7)
4	AB	73.8	84.2 (84.1)
5	ABA	56.8	7.4 (6.7)
6	ABA	78.6	19.3 (18.2)

* BAB=PEO – PS – PEO triblock copolymer ; AB=PEO – PS diblock copolymer ; ABA=PS – PEO – PS triblock copolymer .

** Values quoted in parentheses were calculated with the method of Hermans and Weidinger .

It is seen from the data in Table 3 that the degree of crystallinity in poly (oxyethylene – styrene) block copolymer obtained with the two methods differs from each other at most by 1.1%. This result indicates that equation (6) is reasonable to block copolymers and may therefore be used to the calculation of crystallinity in block copolymer , such as poly (oxyethylene – styrene), in which the scattering of components of crystalline and amorphous in the diffraction pattern can be separated from each other .

It is seen also from the data in Table 3 that the degree of crystallinity in poly (oxyethylene – styrene) block copolymers increases with EO content and decreases in the order : PEO – PS – PEO > PEO – PS > PS – PEO – PS . The existence of such difference is probably due to the following reasons : (1) In addition to the EO content , the lattice distortions and crystallite size in PEO block also affect the crystalline intensity of poly (oxyethylene – styrene) block copolymers . The fact that PEO blocks in BAB block copolymers have higher T_m and sharper melting temperature range^[16] indicates that the crystals in BAB block copolymers are more perfective and have less defects than those in AB and ABA block copolymers . Moreover , the crystallite size in BAB block copolymers is greater than that in AB or ABA block copolymers , for example , the crystallite size of the 1st specimen is 133Å, whereas that of the 3rd is 106Å. So the crystalline scattering intensity of PEO block in BAB is stronger than that of PEO block in AB or ABA block copolymers with approximate EO content and results in higher X_c in BAB block copolymers . (2) In ABA block copolymers amorphous PS block at the two ends of PEO block and the coupling agent toluene diisocyanate in the middle of the block copolymers limit the folding of PEO block , whereas in BAB block copolymers the PEO blocks situated at the two ends of PS block can be folded more freely and easily , thus forming crystals more completely and greatly . (3) Only with the critical value of EO content or higher are there crystalline peaks in diffraction pattern of poly (oxyethylene – styrene) block copolymers . The EO content of the 3rd specimen is 33.5% which approaches to 30%, the critical value of EO content of AB block copolymers . So the crystallinity in it is much lower than that in the 1st specimen whose value of EO content is 37.1% , which is much higher than 20%, the critical value of EO content of BAB block copolymers .

Keywords :

Crystallinity formula , X-ray diffraction , Block copolymers , Poly (oxyethylene - styrene).

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