Isotropic scattering in H_v light scattering from spherulites of polymers

Masato Hashimoto, Akihiko Toda and Hideki Miyaji
Department of Physics, Faculty of Science, Kyoto University, Kyoto 606, Japan
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New results from experiments on light scattering from spherulites of polyethylene and isotactic polystyrene have been obtained. It was found that H_v scattering can be explained well by the sum of the scattering from a perfect spherulite, i.e. a polycrystalline aggregate with radial symmetry, and that from randomly oriented crystallites. The orientation-correlation function of the randomly oriented crystallites has a form of $\exp(-r/a)$, where a is the correlation length, which is about one-sixth of the radius of the spherulite.

(Keywords: polyethylene; polystyrene; spherulite; light scattering; isotropic scattering)

INTRODUCTION

Light scattering is a powerful tool for investigating crystalline texture such as spherulites in solid polymers in the scale of length $\sim 1\ \mu$m. H_v light scattering from spherulites gives a pattern called 'four-leaf clover', which can be qualitatively explained by the model of 'the perfect spherulite', i.e. a polycrystalline aggregate with radial symmetry[1]. However, it is known that the scattering intensity profile cannot be explained by the model. The discrepancy has been studied by several authors and attributed to disorder in spherulites. Keijzers *et al.*[2] introduced a combination model; a spherulite comprises crystallites with radial symmetry and crystallites oriented randomly. Hashimoto *et al.*[3] separated the isotropic scattering from the total scattering and compared the remaining scattering with that of a disordered spherulite. Another approach has been taken by Stein and Chu[4], and Yoon and Stein[5]. They calculated the scattering pattern of spherulites disordered uniformly, without separating the isotropic scattering; the correlation of randomly oriented fluctuation is introduced into 'the perfect spherulite'.

In the present paper, the light scattering from polyethylene (PE) spherulites studied by Hashimoto *et al.* is re-examined first. Secondly, new results on isotactic polystyrene (it-PS) spherulites are reported. Since it-PS can be quenched to the glass during crystallization, isolated spherulites with a spherical shape in the glass can be obtained, which is convenient for comparing scattering experiments with scattering theories. In the next section, the theory of light scattering from a spherulite is briefly reviewed.

THEORY

Perfect spherulite model

The perfect spherulite defined by Stein and Rhodes[1] is a sphere (or a circle in two dimensions) that has different polarizabilities along the radial and tangential directions. In the approximation of Rayleigh and Gans, the intensities of H_v scattering from the perfect spherulite, I_3 for three dimensions and I_2 for two dimensions, are given by the equations[1,6]

$$I_3 = A_3(3/U^3)^2\{(\alpha_t - \alpha_r)(\sin 2\mu)(4\sin U - U\cos U - \mathrm{Si}\,U)/2\}^2 \quad (1)$$

$$I_2 = A_2(1/U^4)[(\alpha_t - \alpha_r)(\sin 2\mu) \times \{2 - 2J_0(w) - wJ_1(w)\}/2]^2 \quad (2)$$

$$U = (4\pi R/\lambda)\sin(\theta/2)$$

$$w = (2\pi R/\lambda)\sin\theta$$

$$\mathrm{Si}\,U = \int_0^U \{(\sin x)/x\}\,\mathrm{d}x$$

where A_3 and A_2 are constants, $J_n(w)$ is the nth Bessel function, α_r and α_t are polarizabilities along the radial and tangential directions, respectively, λ is the wavelength in the medium, μ and θ are azimuthal and polar scattering angles (deg), respectively, and R is the radius of a spherulite. For small-angle scattering, the intensity profile for the two-dimensional model is very similar to that for the three-dimensional model[6]. The intensities should be zero at $\mu = 0$ for both models (see equations (1) and (2)). Experimentally, there is appreciable scattering at $\mu = 0$; the intensity cannot be explained at all by the perfect spherulite model.

Disordered spherulite model

The intensity observed at $\mu = 0$ has been attributed to disorder in spherulites, which breaks the radial symmetry of the perfect spherulite and causes scattering. Stein and Chu[4] calculated the scattering intensity from a two-dimensional spherulite analytically; fluctuations of the optical axis of crystallites with respect to the radius occur in the spherulite. Yoon and Stein[5] calculated the scattering intensity with a computer by using 'the lattice

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Table 1 The weight-average molecular weight (M_w) and polydispersity (M_w/M_n) of the samples used

Code	Material	$M_w/10^4$	M_w/M_n
HDPE$_1$	High density (NBS 1483) polyethylene	3.21	1.11
HDPE$_2$	High density (Sholex 6009) polyethylene	11.4	8.14
it-PS[a]	Isotactic polystyrene	245	3.29

[a] Supplied by Idemitsu Petrochemical Co., Ltd

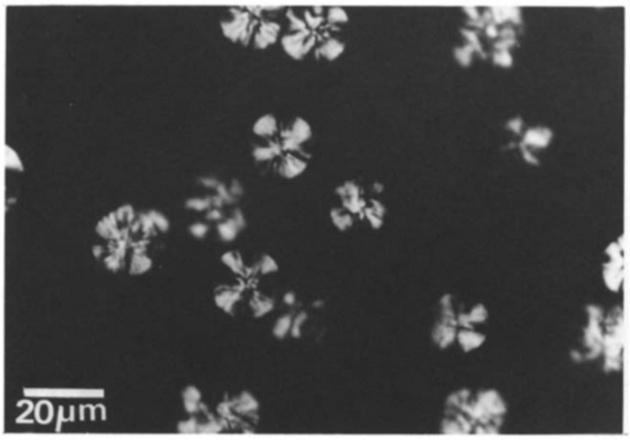

Figure 1 Optical micrograph (crossed polarizers) of spherulites of it-PS crystallized at 180°C for 30 min

theory', in which a two-dimensional spherulite is divided into many cells; the orientation of each cell being determined by the orientations of the two neighbours. However, the intensity predicted by this model at $\mu = 0$ is much smaller than that observed in the present experiment and in the work by Hashimoto *et al.*[3] Further, the calculated intensity profile at $\mu = 0$ has a peak, while experiment shows a monotonic decrease with scattering angle. Therefore, the disordered spherulite model cannot be applied to the spherulite studied here.

Combination model

Keijzers *et al.*[2] introduced a 'combination' model rather simpler than the disordered spherulite model described above; a spherulite contains a certain number of perfectly spherulitic crystallites and a certain number of randomly oriented crystallites. If the interference of the scattering by the two components is neglected, the scattering intensity can be expressed by the sum of the scattering from the perfect spherulites and that from randomly oriented crystallites. 'Randomly oriented crystallites'[7] means that the probability of having two crystallites with correlated orientation depends only upon the distance between them, $|\boldsymbol{r}|$, and is independent of the angle that two crystallites make with the vector, $\boldsymbol{r}$. Keijzers *et al.* used a combination of gaussians as the orientation-correlation function of the randomly oriented crystallites, $f(r)$. Here, a simpler correlation function with a correlation length is proposed. It can be expressed as[8]

$$f(r) = C\exp(-r/a) \tag{3}$$

where C is a constant and a is the correlation length. According to the theory of random walks, the correlation length is given by $a = Kd/\delta^2$, where d is the distance between neighbouring crystallites, δ is the angle of the orientation fluctuation of neighbouring crystallites and K is a constant[8]. The Fourier transformation of equation (3) gives the intensities of the isotropic H_v scattering, I_3^i for three dimensions and I_2^i for two dimensions:

$$I_3^i = A_3^i/\{1 + (ka)^2\}^2 \tag{4}$$

$$I_2^i = A_2^i/\{1 + (ka)^2\}^{3/2} \tag{5}$$

$$k = (4\pi/\lambda)\sin(\theta/2)$$

where A_3^i and A_2^i are constants. It should be noted that isotropic scattering in two dimensions is very different from that in three dimensions, while the intensity profile of the perfect spherulite in two dimensions is similar to that in three.

In the combination model the intensity profile from real spherulites is explained as the sum of the scattering intensity from perfect spherulites (equation (1) or (2)) and that from randomly oriented crystallites in the spherulites (equation (4) or (5)).

EXPERIMENTAL

Details of the samples of PE and it-PS used are listed in *Table 1*. They were melted between two cover-glass slides in vacuum to make films about 100 μm thick. The films of PE were then quenched to room temperature. The spherulites of PE fill the whole sample and are truncated to be polyhedrons. Therefore, the effect of the truncation must be considered, although it has been reported that the effect is not so strong[9].

The films of it-PS were crystallized after self-seeding at 110°C. Spherulites were obtained at 180°C (*Figure 1*). The films of it-PS were then quenched to room temperature in order to freeze the uncrystallized melt into the glass. The freezing is due to the high glass transition temperature (about 90°C) and the slow crystallization rate of it-PS; the radial growth rate[10] has a maximum at 180°C and is 14 μm h^{-1}. Therefore, the spherulites of it-PS are isolated as 'islands' with a spherical shape in the 'sea' of the glass; the situation just corresponds to that assumed in the theoretical model. It is also easy to control the radius of spherulites by changing crystallization time. The radius ranged from 1 μm to 10 μm.

Two-dimensional spherulites of polyethylene were prepared in a thin film 7 μm thick. The film was obtained by casting a xylene solution on a cover-glass slide, evaporating the solvent slowly, melting at 150°C and recrystallizing at about 100°C. Optical microscopy showed that the average diameter of the spherulite is about 20 μm.

The light scattering was performed with a commercial light-scattering photometer (C. N. Wood Mfg. Co. Model 6000). The green line ($\lambda = 546$ nm) through a filter from a mercury lamp (85 W) was used. The incident light was collimated by a pinhole collimator of 1 mm diameter. The detector used was a photomultiplier that can rotate horizontally around a sample to scan scattering angles. The intensity profile of H_v scattering at $\mu = 0$ and 45 was measured, as was the dependence of the intensity on μ at a scattering angle, θ_m, where the scattering intensity becomes maximum in the intensity profile at $\mu = 45$. The angle μ was determined by the intensity of transmitted light without a specimen as

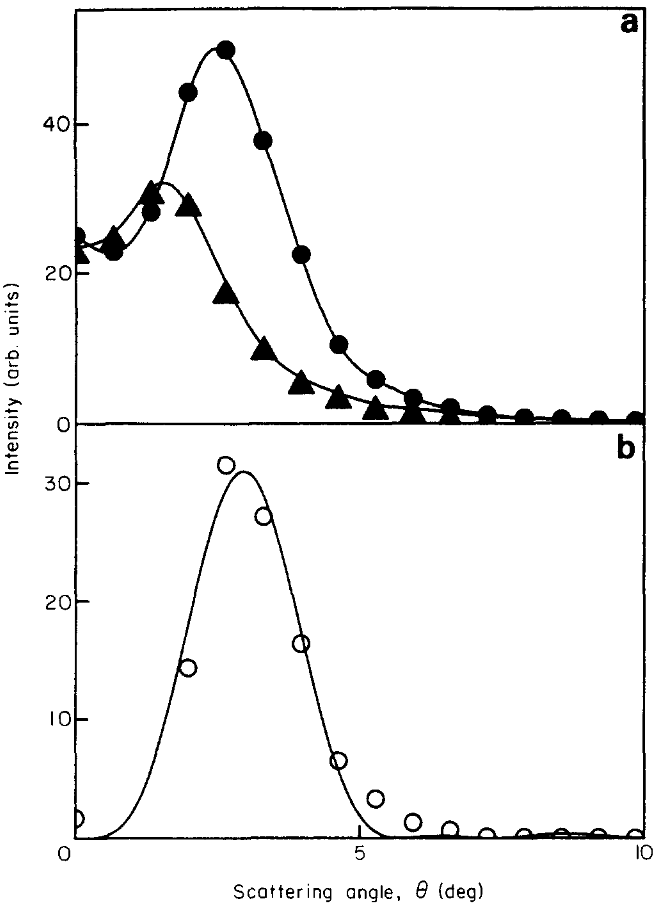

Figure 2 H_v scattered intensity from spherulites versus θ for $HDPE_1$: (a) at $\mu = 45$ (●), $\mu = 0$ (▲) and eye guide (——); (b) a comparison of the theoretical scattering at $\mu = 45$ (- - -) and the experimental values of $I(\mu = 45) - I(\mu = 0)$ (○)

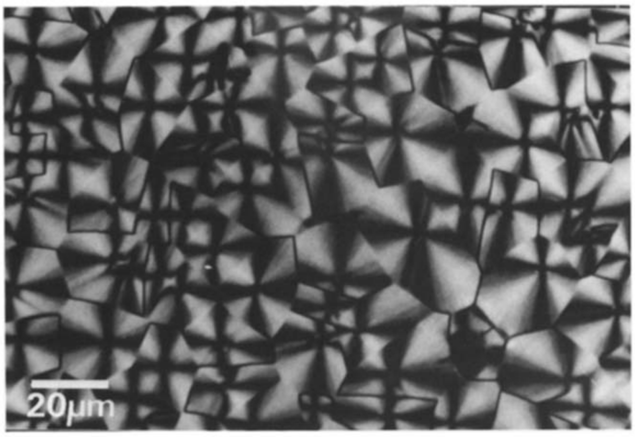

Figure 3 Optical micrograph (crossed polarizers) of spherulites of $HDPE_1$ quenched to room temperature

follows. When the polarizer rotates by an angle of μ from the cross-polarized position, the intensity of transmitted light through the analyser increases following a function proportional to $\sin^2 \mu$. Taking the ratio of the intensity at μ to that at 90°, the value of the angle μ can be determined. For H_v scattering the analyser is rotated so that no transmitted light is observed (cross-polarized).

RESULTS AND DISCUSSION

Figure 2 shows the intensity profile from the $HDPE_1$ spherulites showing a clear Maltese cross under a polarizing microscope (*Figure 3*). The curve cannot be fitted by that of the perfect spherulite model (*Figure 2a*). Furthermore, as shown in this figure, strong scattering is observed at $\mu = 0$; the scattering cannot be explained by either the perfect spherulite model or the disordered spherulite model. It is assumed that the intensity profile of H_v scattering from a real spherulite consists of the part from the perfect spherulite and the isotropic part independent of μ (combination model). First, the difference in the intensities at $\mu = 0$ and at $\mu = 45$ are compared, $I(\theta) = I(\theta, 45) - I(\theta, 0)$. The result is shown in *Figure 2b*; the fitting with the theoretical intensity

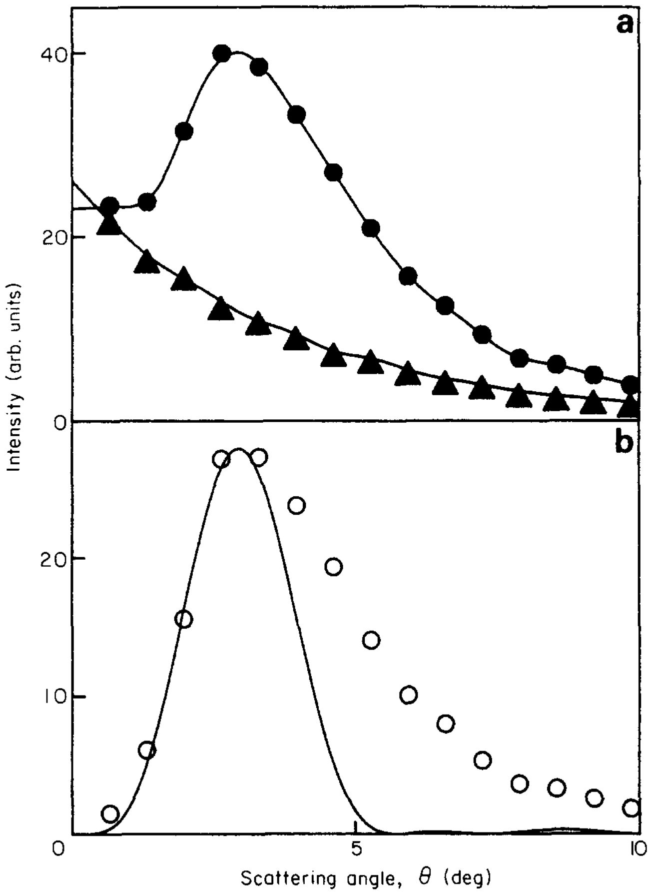

Figure 4 H_v scattered intensity from spherulites versus θ for $HDPE_2$: (a) at $\mu = 45$ (●), $\mu = 0$ (▲) and eye guide (——); (b) comparison of the theoretical scattering at $\mu = 45$ (——) and the experimental values of $I(\mu = 45) - I(\mu = 0)$ (○)

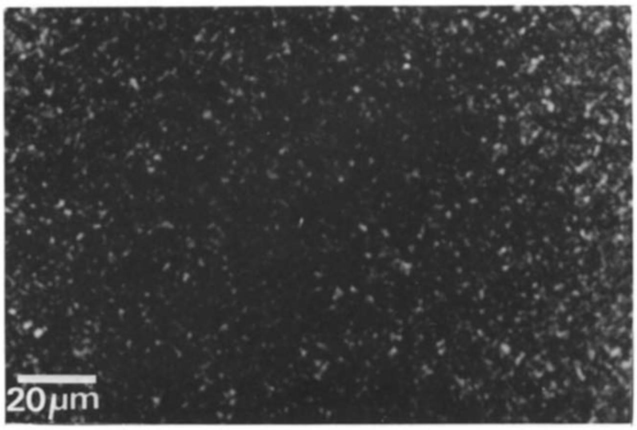

Figure 5 Optical micrograph (crossed polarizers) of spherulites of $HDPE_2$ quenched to room temperature

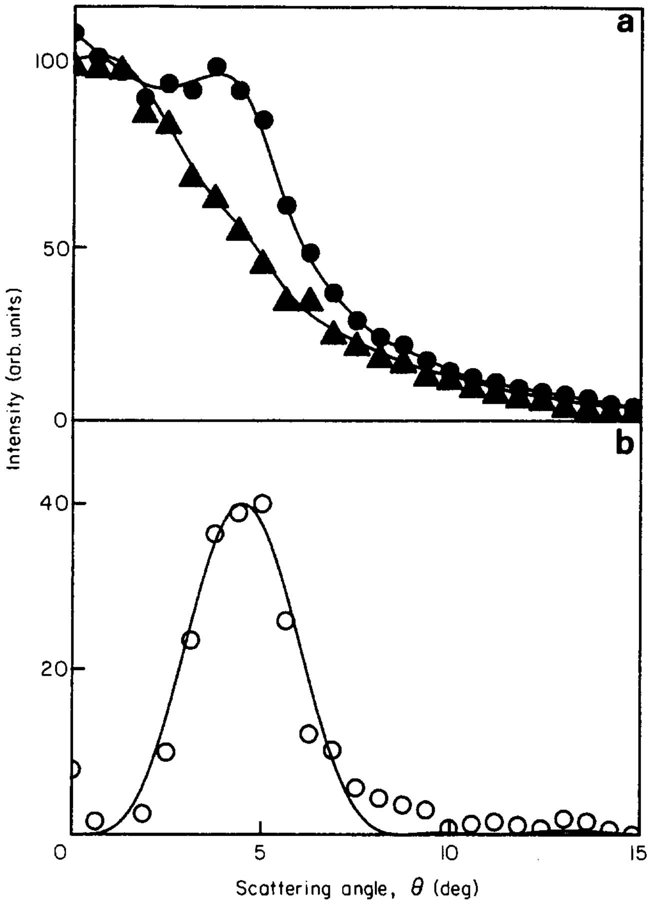

Figure 6 H_v scattered intensity from spherulites of it-PS crystallized at 180°C for 10 min versus θ: (a) at $\mu = 45$ (●), $\mu = 0$ (▲) and eye guide (——); (b) comparison between the theoretical scattering at $\mu = 45$ (——) and the experimental values of $I(\mu = 45) - I(\mu = 0)$ (○)

curve for the perfect spherulite model is good. However, HDPE$_2$ shows a very different intensity profile (*Figure 4*); $I(\theta)$ cannot be fitted by equation (1) or (2). The profile is very similar to that reported by Hashimoto *et al.*[3]. For this sample, a clear Maltese cross cannot be observed under a polarizing microscope (*Figure 5*). Therefore, the deviation from equations (1) and (2) could be due to strong disorder in the spherulites of HDPE$_2$, even if they may be spherulites. For a PE spherulite with a Maltese cross, the deviation of a real spherulite from the perfect spherulite can be attributed only to the isotropic scattering.

The same results on θ-dependence were obtained for H_v scattering from it-PS spherulites showing a Maltese cross (*Figure 6*). Again $I(\theta)$ $(= I(\theta, 45) - I(\theta, 0))$ agrees very well with the theoretical intensity curve for the perfect spherulite model (*Figure 6b*). Therefore, the H_v scattering intensity profile $I(\theta, \mu)$ from a spherulite is expressed as

$$I(\theta, 45) = I_p(\theta, 45) + I_i(\theta, 0) \qquad (6)$$

where $I_p(\theta, \mu)$ is the intensity from the perfect spherulite and $I_i(\theta, 0)$ is intensity at $\mu = 0$. Further, it will be shown that $I_i(\theta, \mu)$ is independent of μ, i.e. isotropic scattering. *Figure 7* shows the dependence of the intensity $I(\theta, \mu)$ on μ at θ_m; the dependence can be fitted well by the equation

$$I(\theta_m, \mu) = B(\theta_m) \sin^2 2\mu + A(\theta_m) \qquad (7)$$

The first term expresses the same μ-dependence as the scattering from the perfect spherulite (equation (1) or (2)). The second term is independent of μ, i.e. the isotropic scattering (equation (4) or (5)). Therefore, the dependence of the intensity on both μ and θ supports the assumption that the H_v scattering is the sum of the scattering from a perfect spherulite and the isotropic scattering.

Finally, the isotropic scattering and the correlation length are to be discussed. It has been assumed that the randomly oriented crystallites in a spherulite cause isotropic scattering and that the orientation-correlation

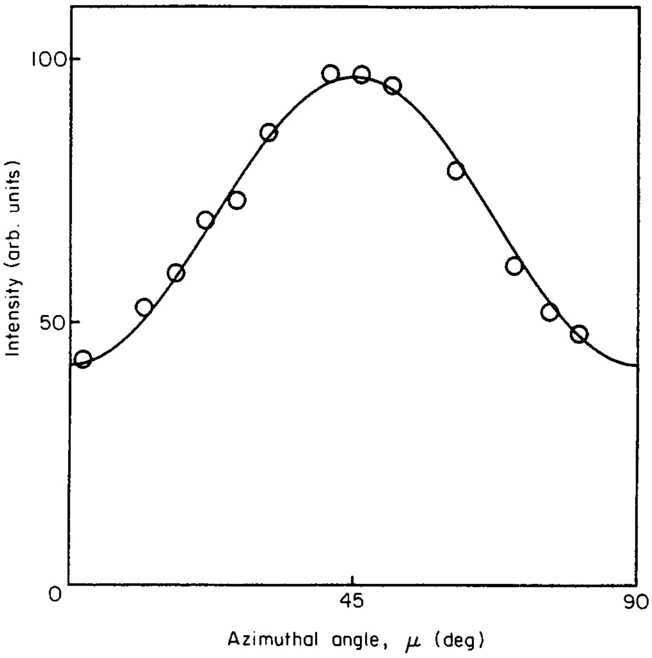

Figure 7 Variation of H_v scattered intensity from spherulites of it-PS crystallized at 180°C for 15 min with μ at θ_m (○) and fitted curve of equation (7) (——)

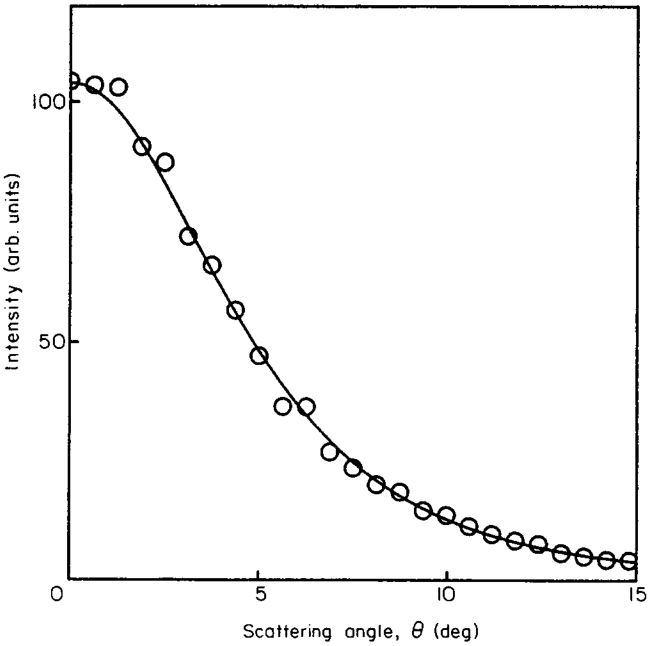

Figure 8 H_v isotropic scattering from spherulites of it-PS crystallized at 180°C for 10 min versus θ: (○) experimental values; (——) values calculated from equation (4)

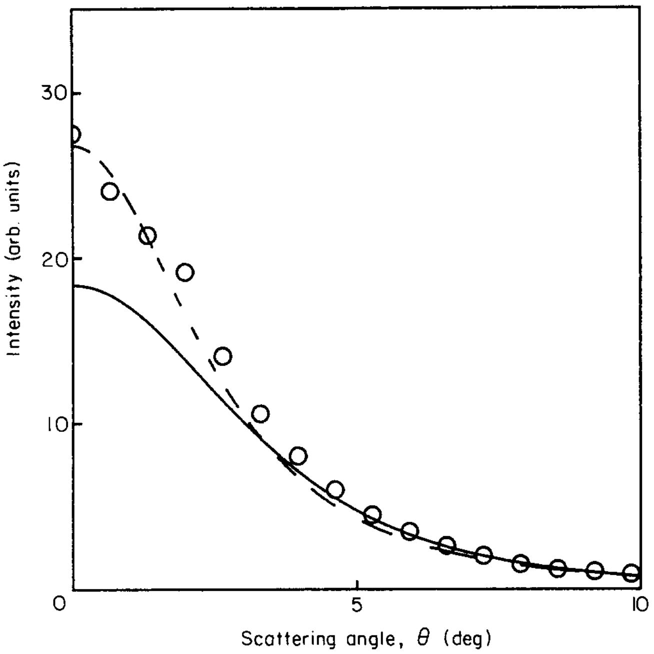

Figure 9 H_v isotropic scattering curve for two-dimensional HDPE spherulites: (○) experimental values; (---) calculated values in two dimensions and (——) three dimensions

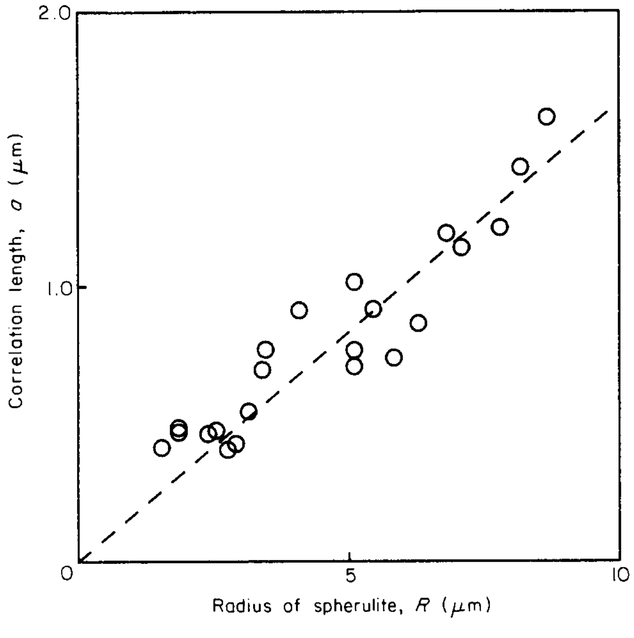

Figure 10 Plot of correlation length versus radius of spherulite of it-PS (○); straight line with a slope of one-sixth (--)

function of the randomly oriented crystallites is given by equation (3). *Figure 8* shows a comparison between observed and calculated (equation (4)) profiles; the agreement is excellent. Further, for two-dimensional PE spherulites confirmed by optical microscopy, the isotropic scattering is again well fitted by equation (5) (*Figure 9*). Therefore, isotropic scattering is found to be caused by crystallites randomly oriented with the orientation-correlation function given by equation (4) or (5). *Figure 10* shows the dependence of the correlation length obtained on the radius of spherulites. The correlation length increases with the radius of a spherulite and is about one-sixth of the radius. Since all the spherulites were crystallized at the same temperature (180°C), the radius is determined only by crystallization time. It is probable that annealing during crystallization time improves the order of the crystallites and/or increases the size of them. The increasing order implies decreasing δ. The increasing size of crystallites implies increasing d. In either case the correlation length, given by $a = Kd/\delta^2$, becomes larger. Hence, annealing may cause the increase in the correlation length.

Let us discuss the origin of the randomly oriented crystallites in a spherulite. It is clear that a real spherulite cannot be a perfect spherulite; in order to fill the spherical space in a spherulite secondary crystal fibrils should branch off from primary ones growing in the radial direction. These branches break the radial symmetry of a spherulite and give rise to additional scattering to the scattering from a perfect spherulite. In the present analysis, it has been shown that the additional scattering can be described as isotropic scattering. The analytical model that relates the correlation length to the branching of fibrils is required for further analysis.

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