

WAXD STUDY OF POLYMORPHOUS ISOTACTIC-POLYPROPYLENE BY COMPUTER PEAK-RESOLUTION METHOD*

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ABSTRACT

Polymorphous i-PP containing α and β phases were studied by WAXD and computer peak-resolution method (CPRM). The asymmetric Gaussian-Cauchy functions (a-GC) were adopted to fit the profiles of both amorphous and crystalline peaks. For the crystalline peaks, the fitting results of a-GC are better than the symmetric-GC; for the amorphous peaks, they are better than polynomial and exponential functions, etc. Using the retarded least-square procedure (RLSP) on microcomputer the results of peak-resolution are rather satisfactory. For the polymorphous samples containing α and β phases, the relations between phase-state, crystallinity, crystalline size, the ratio of α, β relative content and the crystallization temperature T_c were studied by CPRM. The ratio of α, β relative contents obtained by CPRM and Turner-Jones eq. have been carefully compared. There are many improvements in this work. A simple estimation method of WAXD peak areas, both for amorphous and crystalline peaks, is suggested.

INTRODUCTION

In the polymer systems, i-PP is a typical example which can form polymorphous phases. In various crystal types of i-PP, except that α -type can exist along in amorphous phase^[1,2], β, γ and smectic types often coexist with α -type in the amorphous phase. α -type crystal had been studied extensively^[1-6], but β -type was less reported^[1,2,7-17], and γ -type even less studied^[18,19]. Many methods and instruments can be used to observe and detect the α and β crystal directly, e.g. electron microscope, polarizing microscope and DSC are commonly used, but due to the limitations of these methods, they can not be used for quantitative analysis. WAXD-CPRM have been used for phase analysis of polymer systems only containing one crystal type with very good results^[20-23]. But it has not been used in the polymorphous systems. In this paper, WAXD-CPRM is used to study polymorphous systems containing α and β crystal types, the results indicate that CPRM is an adequate and efficient method to study the polymorphous systems quantitatively.

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EXPERIMENTAL

1. Sample

(1) Amorphous sample: Two amorphous samples A-FD and A-IOC were prepared by purifying a-PP provided by Fudan University and Institute of Organic Chemistry, Academia Sinica (IOC-AS) respectively.

(2) Crystalline sample: Two kinds of i-PP, one of which β -nucleator was added (provided by IOC-AS, $\bar{M}_n = 4 \cdot 10^5$; NMR determination, isotactic), were melted at $210^\circ \pm 10^\circ \text{C}$ for 3 min., then immersed into glycerine bath for 2 hrs at various temperatures ($T_c = 100^\circ, 110^\circ, 120^\circ, 130^\circ, 135^\circ, 140^\circ \pm 0.2^\circ \text{C}$) to render isothermal crystallization, two series of α - T_c and β - T_c were prepared.

2. WAXD

Japan Rigaku 2077-type X-Ray Diffractometer were used, Cu target, Ni filter, $2\theta: 10^\circ - 25^\circ$, which is the range of main peaks group. After corrections of the air scattering, polarization factor and Compton scattering, etc., the intensities $I(2\theta)$ were conveyed into PDP 11/03 microcomputer and the peaks were separated by RLSP.

PEAK-RESOLUTION METHOD

1. Selection of characteristic functions

Owing to the effects of sample forms, instrument performances and experimental conditions, the crystalline peaks are asymmetric, especially in the range of small angle 2θ ; and due to the structure of amorphous phase, its diffraction peak are also asymmetric, the authors choose the asymmetric Gaussian-Cauchy functions (a-GC) as the characteristic functions for both amorphous and crystalline peaks [20,24]. For the crystalline peaks, the results are better than that of symmetric-GC functions. For amorphous peaks, we compare a-GC Y_1 with polynomial Y_2 [20,21], exponential Y_3 and Y_4 [25,26]. If five parameters are adopted for these four functions, the fitting results indicate that a-GC is the best (Fig. 1 and Table 1), i.e. the peaks

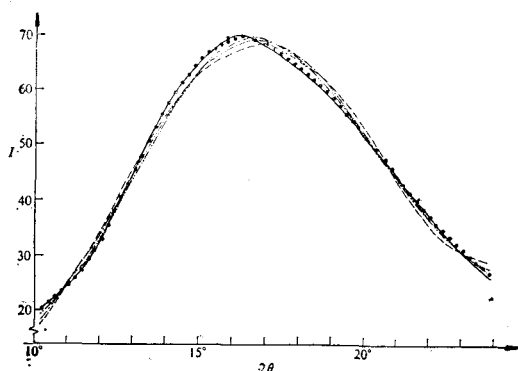


Fig. 1 Comparison of the fitting results between various characteristic functions and amorphous diffraction peak

..... Experimental — Y_1 ; ---- Y_2 ; -.-.- Y_3 ; Y_4

are at the correct positions, errors are the smallest and the meaning of parameters are obvious. Furthermore when a-GC are selected as the characteristic functions of both amorphous and crystalline peaks, the calculation program can be simplified.

Table 1 Comparison of various amorphous characteristic functions*

Peak parameter Characteristic function	A_a	w_{la}	w_{ra}	F_a	P_a	$\delta(\%)^{***}$
$Y_1^{**} = F \cdot G + (1 - F) \cdot C$	69.87	7.88°	12.68°	0.2673	16.0°	1.3

Peak parameter Characteristic function	a_0	a_1	a_2	a_3	a_4	P	$\delta(\%)$
$Y_2 = \sum_{i=0}^4 a_i x^i$	722.4	-220.4	23.81	-1.041	$1.589 \cdot 10^{-2}$	16.6°	2.9
$Y_3 = \exp(\sum_{i=0}^4 a_i x^i)$	0.4835	-0.360	0.116	$-1.30 \cdot 10^{-3}$	$1.154 \cdot 10^{-4}$	16.6°	2.2
$Y_4 = \exp(\sum_{i=0}^4 a_i x^i)$	-1.000	0.2603	$-6.77 \cdot 10^{-3}$	$5.38 \cdot 10^{-4}$	$-1.244 \cdot 10^{-5}$	16.8°	2.9

* The data are from reference (25), the observed peak position $P=16.2^\circ$.

** G, Gaussian function; C, Cauchy function; A_a , amorphous peak height; w_{la} and w_{ra} , left and right full width at half-maximum; F_a , compound factor; P_a , peak position.

*** $\delta\%$, the fitting error, eq. (1).

2. Peak-resolution calculation method

In order to make peak-resolution, several optimum methods, i.e. 0.618, Monte Carlo, Simplex and Retarded least-square Procedure, were compared, the last one (RLSP) is the best method to treat the problem of large number variables. The fitting error of peak-resolution is

$$\delta\% = \sqrt{\frac{s}{\bar{s}}} \cdot 100\% \quad (1)$$

where

$$s = \sum_{i=1}^n (I_{\text{calc}} - I_{\text{obs}})^2$$

$$\bar{s} = \sum_{i=1}^n (I_{\text{obs}})^2 \quad (2)$$

n is the numbers of points taken from $2\theta=10^\circ-25^\circ$, I_{calc} and I_{obs} are fitting and observed diffraction intensities respectively.

RESULTS AND DISCUSSION

1. Peak resolution results

By means of RLSP, the peak-resolution results of α - T_c , β - T_c and smectic samples^[25] are rather satisfactory (Fig. 2). It shows that CPRM is an adequate method to study the polymorphous systems quantitatively. It is especially effective to separate the heavy overlapping peaks.

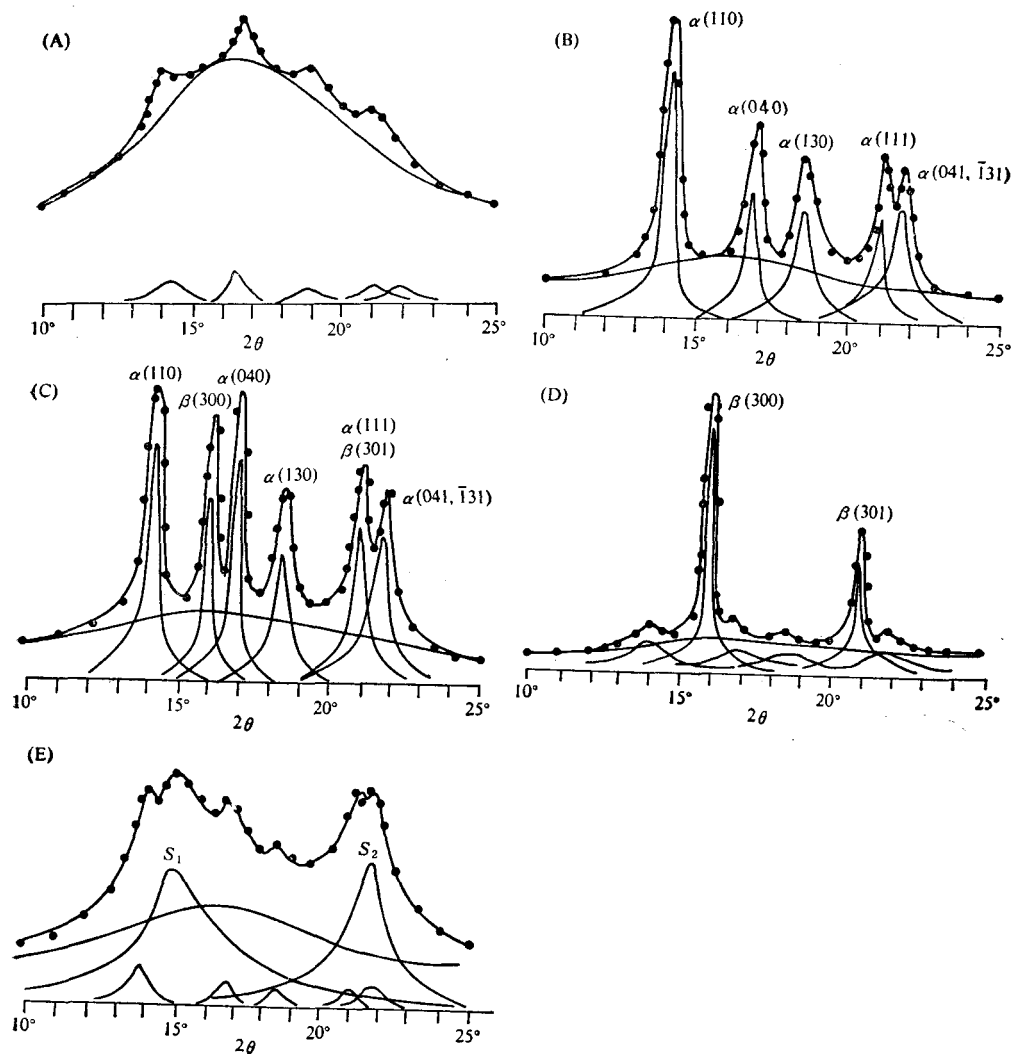


Fig. 2 The separation results of WAXD of various polymorphous i-PP

(A), (B) α +amorphous (α - T_c series),
 (C), (D) α + β +amorphous (β - T_c series),
 (E) α +smectics+amorphous

..... Observation
 — Calculation

2. Amorphous peak parameters

There are many procedures to estimate the amorphous diffraction from WAXD of crystalline i-PP^[4, 20-23]. CPRM results show that for the β - T_c series of different crystallinities and different α , β relative contents, the amorphous parameters P_a , w_{Ia} , w_{ra} , F_a are essentially unchanged except A_a ; while $P_a = 16.2^\circ$, which agrees with the reference data (Table 2)^[25, 28].

Table 2 Comparison of amorphous peak parameters of α -PP and α - T_c series

Peak parameter Sample	A_a	P_a	w_{la}	w_{ra}	F_a	S_{ao}	$\delta(\%)^{**}$
A-FD*	100*	16.38°	9.56°	13.34°	-0.542	10.45	2.9
A-IOC*	100	15.92°	9.46°	13.48°	-0.586	10.54	3.2
β -100	5.72	16.71°	10.25°	13.46°	-0.618	10.56	2.6
β -110	4.35	16.12°	10.07°	13.16°	-0.511	10.49	1.9
β -120	3.96	16.00°	10.03°	13.04°	-0.609	10.44	2.9
β -130	1.86	15.98°	10.02°	13.01°	-0.506	10.45	2.2
β -135	3.35	16.08°	10.04°	13.07°	-0.596	10.45	2.3
β -140	3.67	16.32°	10.06°	13.10°	-0.589	10.47	1.8
Average value		16.19°	9.94°	13.21°	-0.570	10.49	2.5

* A_a of amorphous samples A-FD and A-IOC are normalized, let $A_a=100$.

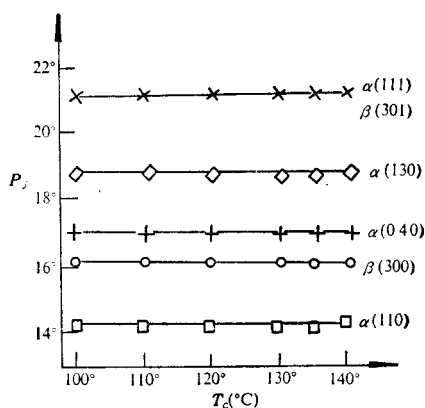
** $\delta\%$ is the total fitting error, containing crystalline peaks.

According to this, the calculation of the areas of amorphous peaks can be simplified as follows

$$S_a = A_a \cdot S_{ao} (2\theta_0, 2\theta_p, F_a, P_a, w_{la}, w_{ra}) \quad (3)$$

$$S_{ao} = \int_{2\theta_0}^{2\theta_p} \left\{ F_a \cdot \exp \left[-\ln 2 \left(2 \frac{2\theta - P_a}{w_a} \right)^2 \right] + (1 - F_a) \left[1 + \left(2 \frac{2\theta - P_a}{w_a} \right)^2 \right]^{-1} \right\} d(2\theta) \quad (4)$$

If $2\theta_0=10^\circ$, $2\theta_p=25$, and F_a , P_a , w_{la} , w_{ra} taken from Table 1 are substituted into eq. (4), we obtain $S_{ao}=10.5$. Once A_a is estimated, S_a can be calculated easily.

**Fig. 3** The relations between P_j and T_c

3. Crystalline peak parameters

(1) Peak position parameter P_j ; Fig. 3 shows that β - T_c series are polymorphous i-PP containing α and β phases. As T_c increases, P_j keeps unchanged, i.e. the parameters of unit cell are essentially constant.

(2) Compound factor F_j : Fig. 4 shows that in the β - T_c series, $F_\alpha \doteq F_\beta > F_a$. This results agree with Hindeleh's conclusion, i.e. F is related to the order of molecular chains^[20].

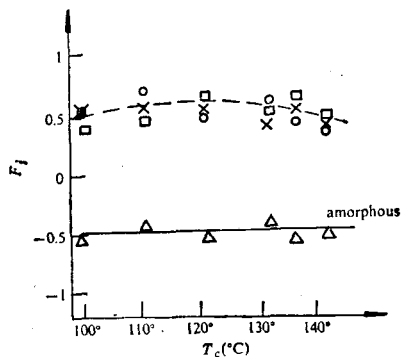


Fig. 4 The relations between F_j and T_c

○ β (300); × α (111); + β (301); □ α (110)

(3) Full width at half-maximum w_j : Fig. 5 shows that the dependence of the apparent crystallite size L_j calculated from w_j on T_c . It indicates that as T_c increases. The change in $L_\alpha(110)$, $L_\alpha(130)$ and $L_\alpha(041, \bar{1}31)$, etc., is very small; the change in $L_\alpha(040)$ seems rather complicated, but the weak peak $\alpha(040)$ is strongly affected by the main peak $\beta(300)$, so these data are only serving as references. Minimum of $L_\beta(300)$ appear near $T_c = 120^\circ\text{C}$; $L_\alpha(111) + \beta(301)$ is the average of α and β crystallites size, below 120°C its change is smaller, above 120°C it increases gradually, which might reflect the change in β -crystallites. In short, the reorganization of β -crystallites is more easily observed than that of α in the range of T_c .

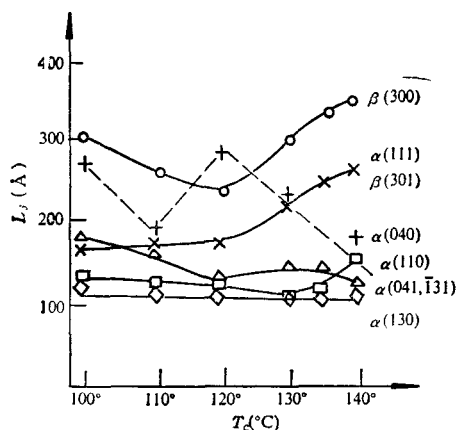


Fig. 5 The relations between L_j and T_c

(4) Peak height parameter A_j : From A_j the peak area S_j can be calculated by eq. (3). From S_j , the relative content of each phase in the polymorphous system can be calculated by the following eq.^[4]

$$X_\alpha \% = \frac{\sum_{\alpha, j} S_{\alpha, j}}{\sum_{\alpha, j} S_{\alpha, j} + \sum_{\beta, j} S_{\beta, j} + S_a} \cdot 100 \% \quad (5)$$

$$X_{\beta}\% = \frac{\sum_{\beta,j} S_{\beta,j}}{\sum_{\alpha,j} S_{\alpha,j} + \sum_{\beta,j} S_{\beta,j} + S_a} \cdot 100\% \quad (6)$$

$$X_{\alpha}\% = \frac{S_a}{\sum_{\alpha,j} S_{\alpha,j} + \sum_{\beta,j} S_{\beta,j} + S_a} \cdot 100\% \quad (7)$$

when eq. (5)–(7) are used, two points must be cited: first, for $2\theta = 10^\circ - 25^\circ$, the contribution of the main peaks (hk0) and (hk1) is only considered in j . Second, it happens that $\alpha(111)$ and $\beta(301)$ overlap at $2\theta = 21^\circ$, they are not separated by CPRM, so another method to separate them must be devised. In α - T_c series which only contains α -phase, the ratio K_r can be calculated by the following eq.

$$K_r = \frac{S_{\alpha(111)}}{S_{\alpha(110)} + S_{\alpha(040)} + S_{\alpha(130)}} \quad (8)$$

where $S_{\alpha(110)}$, $S_{\alpha(040)}$, $S_{\alpha(130)}$ and $S_{\alpha(111)}$ of α - T_c series are obtained by CPRM. The average value $\bar{K}_r = 0.25$. Then $\alpha(111)$ and $\beta(301)$ can be separated by using $\bar{K}_r$, as follows.

$$\begin{aligned} \sum_{\alpha,j} S_{\alpha,j} &= S_{\alpha(110)} + S_{\alpha(040)} + S_{\alpha(130)} + S_{\alpha(111)} + S_{\alpha(041, \bar{1}31)} \\ &= (1 + \bar{K}_r) (S_{\alpha(110)} + S_{\alpha(040)} + S_{\alpha(130)}) + S_{\alpha(041, \bar{1}31)} \end{aligned} \quad (9)$$

$$\begin{aligned} \sum_{\beta,j} S_{\beta,j} &= S_{\beta(300)} + S_{\beta(301)} \\ &= S_{\beta(300)} + S_{\alpha(111) + \beta(301)} - \bar{K}_r [S_{\alpha(110)} + S_{\alpha(040)} + S_{\alpha(130)}] \end{aligned} \quad (10)$$

Substituting eq. (9), (10) and (4) into (5)–(7), the content of each phase can be obtained. Fig. 6 shows that in the β - T_c series, α -phase always exists and its contents are about 10%; the contents of β -phase are higher than that of α ; as T_c increases, the change of β -phase content is opposite to that of amorphous, it is possible that in the range of T_c , the transformation between β -phase and amorphous phase occurs; the best crystallization temperature of β 's is at 130°C , where $X_{\beta}\% = 50\%$.

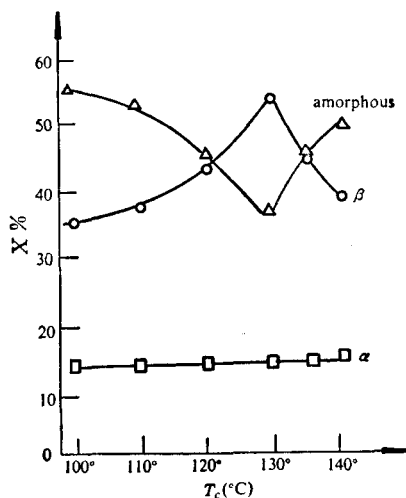


Fig. 6 The relations between $X\%$ and T_c

4. α, β relative content ratio k and Turner-Jones equation

The definition of α, β relative content ratio k is

$$k = \frac{\sum_{\beta, j} S_{\beta, j}}{\sum_{\alpha, j} S_{\alpha, j} + \sum_{\beta, j} S_{\beta, j}} \quad (11)$$

Fig. 7 shows the change of k versus T_c . The results indicate that at 130°C , the content of β -phase is maximum, and $k \approx 0.83$.

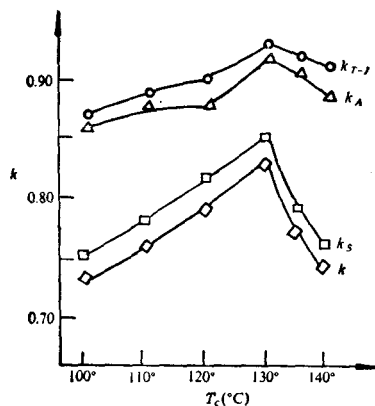


Fig. 7 The relations between k and T_c

Turner-Jones introduced an equation to estimate α, β relative content ratio, and this equation has been widely used [2, 12, 13]. But except the restraint of 2θ range, there are three weak points in the Turner-Jones equation: first, the cancellation of amorphous peak is arbitrary; second, after cancellation, the peak heights H_α and H_β instead of the peak areas are used to calculate the relative content ratio; third only (hk0) crystal planes are considered. If we only consider the contribution of (hk0) crystal planes, there are three expressions of α, β relative content: Turner-Jones peak height

$$k_{T-J} = \frac{H_{\beta(300)}}{H_{\alpha(110)} + H_{\alpha(040)} + H_{\alpha(130)} + H_{\beta(300)}} \quad (12)$$

CPRM peak height

$$k_A = \frac{A_{\beta(300)}}{A_{\alpha(110)} + A_{\alpha(040)} + A_{\alpha(130)} + A_{\beta(300)}} \quad (13)$$

CPRM peak area

$$k_s = \frac{S_{\beta(300)}}{S_{\alpha(110)} + S_{\alpha(040)} + S_{\alpha(130)} + S_{\beta(300)}} \quad (14)$$

Fig. 7 shows that the tendency of k_{T-J} versus T_c is similar to that of k_A and k_s , but $k_{T-J} \approx k_A > k_s \approx k$. k_{T-J} is larger than k about 10%. The reason is that the peak area is proportional to the product of peak height and FWHM, i.e. by integrating eq.(4) we can obtain the following equation

$$S_j = \frac{1}{2} \left[F_j \sqrt{\frac{\pi}{\ln 2}} + (1 - F_j) \pi \right] A_j \cdot w_j = K_F \cdot A_j \cdot w_j \quad (15)$$

for crystalline peak $F_j \doteq 0.5$. So S_j not only depends on A_j but also on w_j , while the latter is not a constant but affected by crystalline size, crystalline distribution and lattice distortion, etc. Hence only using peak height H to estimate α, β relative content ratio is merely an approximation. However, for simplicity, if we use k_s as an approximation of k , the difficulty of separation of (111) from (301) may be avoided.

CONCLUSION

1. WAXD-CPRM is an adequate and efficient method for quantitative study the polymorphous systems.

2. a-GC functions are good characteristic functions of both amorphous and crystalline peaks, its parameters have the obvious meaning, so they can be used for structure analysis, and the calculation is very simple.

3. For the polymorphous i-PP containing α and β phases, the calculation of α, β relative content ratio k by CPRM is better than that from Turner-Jones equation.

4. A study of the polymorphous i-PP by CPRM shows that at that from $T_c = 100^\circ - 140^\circ \text{C}$, both α and β phases coexist, but as T_c increases, the change of α -phase content and α -crystallite size is very small, but in β -phase it is very obvious, and the change of β -phase content is in opposite direction to that of amorphous'. The optimum temperature of β -crystallization is at $T_c = 130^\circ \text{C}$.

5. A convenient estimation method of peak area of each phase in WAXD is suggested.

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Appendix

A Simple Estimation Method of Peak Areas in WAXD

1. Crystalline peak

According with experimental and eq. (15), the change of S_j versus $A_j \cdot w_j$ of $\beta-T_c$ series is plotted in Fig-A. Fig-A shows that although crystallinity and α, β relative content of the samples are different, (hk0) and (hk1) crystal planes are considered, the experimental points are on a straight line, the slope is equal to 1.3. If we get $F_j = 0.5$, from eq. (15) we can obtain

$$K_F = \frac{1}{2} \left[F_j \sqrt{\frac{\pi}{\ln 2}} + (1 - F_j) \pi \right] = 1.3 \quad (\text{A})$$

which agrees with the experimental. So having obtained A_j and w_j , S_j can be estimated by the following eq.

$$S_j = 1.3 A_j \cdot w_j \quad (\text{B})$$

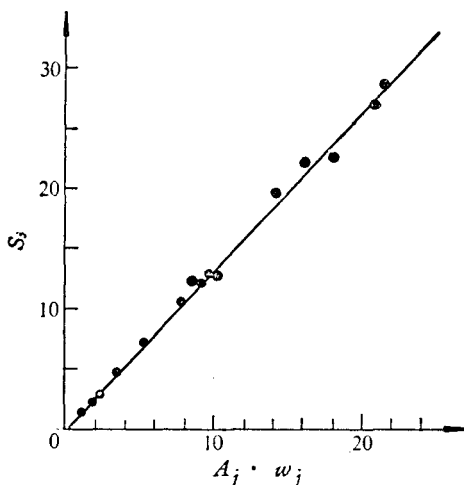


Fig-A The relations between S_j and A_j, w_j

2. Amorphous peak

From eq.(3) amorphous peak area is

$$S_a = A_a \cdot S_{a0} \quad (\text{C})$$

then we should estimate A_a and S_{a0} respectively.

(1) Estimation of A_a : Because the crystalline peaks of crystallization samples are heavy overlapping with amorphous peak, the measurement of A_a is difficult. But we can find a certain 2θ , where no overlap between crystalline peak and amorphous peak occurs. We take such a position $2\theta = 31.8^\circ$, and the intensities are $I(31.8^\circ)$. If the character of the amorphous peak of various samples does not change, $A_a(16.2^\circ)$ should be proportional to $I(31.8^\circ)$, i.e.

$$K_a = \frac{A_a(16.2^\circ)}{I(31.8^\circ)} \quad (D)$$

Plotting $A_a(16.2^\circ)$ versus $I(31.8^\circ)$ of α - T_c and β - T_c series, the points correspond to a straight line (Fig-B), the slope $K_a=3.13$, so

$$A_a(16.2^\circ) = 3.13 \cdot I(31.8^\circ) \quad (E)$$

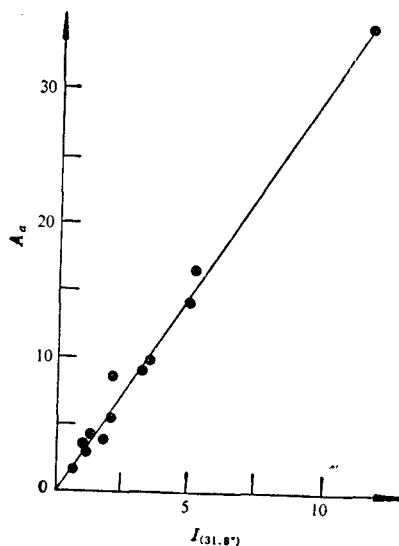


Fig-B The relations between $A_a(16.2)$ and $I(31.8)$

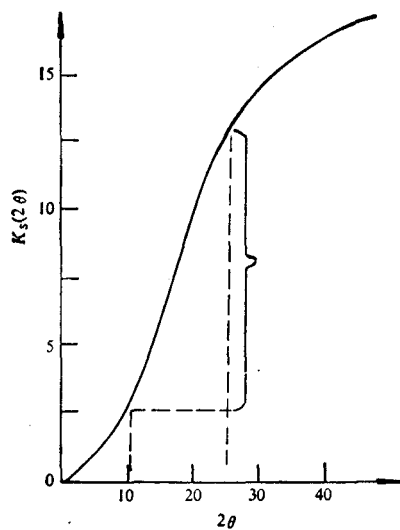


Fig-C The relations between $K_s(2\theta)$ and 2θ

(2) Estimation of S_{a_0} :

$$K_s(2\theta) = \int_0^{2\theta} I_{a_0}(2\theta) d(2\theta) \quad (F)$$

let

then

$$S_{ao} = \int_{2\theta_0}^{2\theta_p} I_{ao}(2\theta) d(2\theta) = k_s(2\theta_p) - k_s(2\theta_0) \quad (G)$$

where $I_{ao}(2\theta)$ is the a-GC functions with $A_a=1$. Substituting amorphous peak parameters in Table 2 into eq. (G) and using Simpson integration, the relations of $k_s(2\theta)$ versus 2θ can be obtained (Fig-C). Thus S_{ao} can be estimated by Fig-C and eq. (4).

Therefore S_a can be obtained from A_a and S_{ao} at once

$$S_a = 3.13 \cdot I(31.8^\circ) \cdot [K_s(2\theta_p) - K_s(2\theta)] \quad (H)$$

Eq. (B) and eq. (H) are the simple estimation equations of crystalline and amorphous peak areas respectively.