General procedure for evaluating apparent crystallinity and substantial crystallinity from WAXS patterns of binary and ternary copolymers

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By defining a total correction factor *Fa* for the WAXS curves of amorphous homopolymers, a new method for the resolution between overlapping WAXS curves is proposed and used to evaluate the apparent crystallinity relative to the entire sample and the substantial crystallinity relative to the poly(ethylene oxide) grafts alone in polystyrene–graft-poly(ethylene oxide) binary copolymers. By introducing the concept of 'amorphous matrix', the same method is also used to evaluate the two kinds of crystallinities in poly(*n*-butyl acrylate–acrylic acid)–graft-poly(ethylene oxide) ternary copolymers. Both apparent crystallinity and substantial crystallinity increase with increasing poly(ethylene oxide) content, but the substantial crystallinity can characterize the effects of the backbone chains on the crystallization of the poly(ethylene oxide) grafts more distinctly and more reasonably than the apparent crystallinity.

(Keywords: total correction factor; apparent crystallinity; substantial crystallinity; WAXS; binary copolymer; ternary copolymer)

INTRODUCTION

The physical and mechanical properties of polymers are profoundly dependent on the degree of crystallinity. Among the techniques used for determining polymer crystallinity, wide-angle X-ray scattering (WAXS) methods play a dominant role[1]. In previous studies, most of the WAXS methods[2–8] for determining crystallinity have been applied to homopolymers, but not to copolymers.

Recently, the author proposed an improved WAXS method for evaluating the apparent crystallinity in poly(ethylene oxide)–block-polystyrene copolymers[9] and poly(methyl acrylate)–graft-poly(ethylene oxide)[10]. The same method was also used to evaluate the apparent crystallinity in poly(methyl methacrylate)–graft-poly(ethylene oxide) copolymers and their ionic complexes with $LiClO_4$, KSCN and $FeCl_2$, as well as a graphical multiple halo resolution method[11]. In the second case, the substantial crystallinity in poly(ethylene oxide) grafts alone was also evaluated after the graphical resolution between the overlapping haloes. The author has also studied the crystallinity in the chlorinated polyethylene from solid-phase chlorination, using an iterative method[12].

In this paper, a new method of resolving the overlapping WAXS intensities of different amorphous polymers is described and used to evaluate the apparent crystallinity relative to the entire sample (*Xca*) in polystyrene–graft-poly(ethylene oxide) binary copolymers (PS–g-PEO) and poly(*n*-butyl acrylate–acrylic acid)–graft-poly(ethylene oxide) ternary copolymers (P(BA-AA)–g-PEO). The substantial crystallinity relative to the PEO grafts alone of the two kinds of copolymers is also evaluated at the same time.

EXPERIMENTAL

Materials

The PS–g-PEO copolymers were synthesized by copolymerization of styrene (S) with PEO macromers. The P(BA–AA)–g-PEO copolymers were synthesized by copolymerization of *n*-butyl acrylate (BA) and acrylic acid (AA) with PEO macromers. The copolymers were purified by three extractions with a mixture of ethyl ether and acetone (3:7 by volume), followed by three with water. After evaporation under an infra-red lamp, the purified copolymers were dried in a vacuum desiccator at 50°C for 2 days, and were then characterized by i.r. and ^{1}H n.m.r. spectroscopies.

Wide-angle X-ray scattering (WAXS)

The WAXS patterns were obtained using a Rigaku 3015 diffractometer giving 35 kV nickel-filtered Cu Kα radiation at 25 mA. The diffractometer was equipped with Soller slits, a divergence slit (1°), a receiving slit (0.15 mm), and a scattering slit (1°). At room temperature, scanning was performed at a rate of 2° min^{-1} from 2° to 90° for the homopolymers PEO, PS, PBA and PAA, and from 2° to 35° for the copolymers. All samples were tested in the form of slabs about 2 mm thick.

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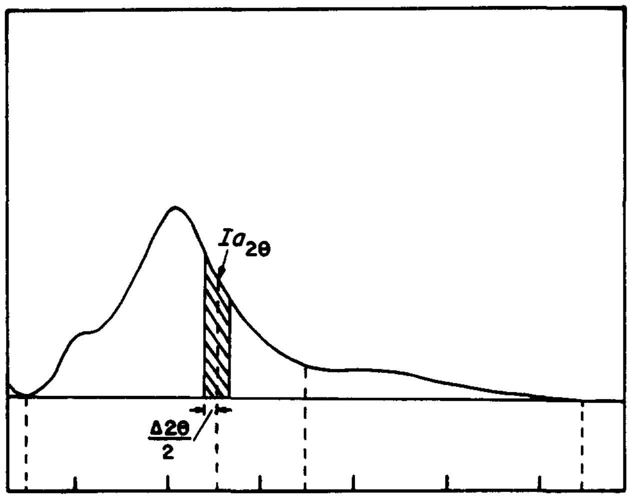

Figure 1 Diagram for calculating the total correction factor Fa. $2\theta_0$ = lower terminal angle of the whole amorphous scattering curve; $2\theta_t$ = upper terminal angle of the whole amorphous scattering curve; $2\theta_p$ = initial angle of scanning; $\Delta 2\theta$ = angular interval; 2θ = angle at the intermediate point of the angular interval; $Ia_{2\theta}$ = relative integrated intensity in the range from $2\theta - \Delta 2\theta/2$ to $2\theta + \Delta 2\theta/2$

Evaluation of crystallinity from the WAXS patterns of copolymers

On the basis of the theory described previously[11], an improved formula for the apparent crystallinity (Xca) in copolymers can be proposed as follows:

$$Xca = \frac{\sum_i^M \sum_j^N Fc_{ij} \cdot Ic_{ij}}{\sum_i^M \sum_j^N Fc_{ij} \cdot Ic_{ij} + \sum_i^M Fa_i \cdot Ia_i + \sum_k^P Fa_k \cdot Ia_k} \times 100\% \tag{1}$$

where Ic_{ij} and Ia_i are respectively the relative integrated intensities of the major crystalline peaks and the amorphous scattering curve of semicrystalline component i over the partial angular range, Ia_k is the relative integrated intensity of the amorphous scattering curve of amorphous component k over the partial angular range, M is the number of semicrystalline components, P is the number of amorphous components, N is the number of the major crystalline peaks of semicrystalline component i, and Fc_{ij} is the total correction factor for the crystalline peaks, which is defined by

$$Fc_{ij} = C_{ij}/Kc_i \tag{2}$$

in which

$$C_{ij}^{-1} = f^2 \cdot \mathrm{e}^{-2B(\sin\theta/\lambda)^2} \cdot \frac{1 + \cos^2 2\theta}{\sin^2\theta\cos\theta} \cdot A \tag{3}$$

where f is the atomic scattering factor of unit mass, θ is the Bragg angle, λ is the X-ray wavelength, $\mathrm{e}^{-2B(\sin\theta/\lambda)^2}$ is a temperature factor (and $2B = 10$), $(1 + \cos^2 2\theta)/(\sin^2\theta\cos\theta)$ is the Lorentz polarization factor, and A is the absorption factor. For slab samples of sufficient thickness, the absorption factor A can be omitted from equation (3).

Kc_i is a constant used to correct the reduced integrated intensity due to collection of the intensity of major crystalline peaks only. Let T be the total number of crystalline peaks of semicrystalline component i; then

$$Kc_i = \sum_j^N C_{ij} \cdot Ic_{ij} \Big/ \sum_j^T C_{ij} \cdot Ic_{ij} \tag{4}$$

For convenience, the WAXS pattern of the amorphous polymer concerned is regarded as a whole scattering curve rather than several overlapping haloes. We first define a partial weighted average correction factor, which can be derived from *Figure 1*. In this figure, the whole scattering curve of the amorphous homopolymer concerned lies between $2\theta_o$ and $2\theta_t$. Dividing the whole integrated intensity into several parts with equal angular interval $\Delta 2\theta$, the partial weighted average correction factor $\bar{C}_p$ can be written as follows:

$$\bar{C}_p = \frac{\sum_{2\theta = 2\theta_o}^{2\theta_p} C_{2\theta} \cdot Ia_{2\theta}}{\sum_{2\theta = 2\theta_o}^{2\theta_p} Ia_{2\theta}} \tag{5}$$

in which

$$C_{2\theta}^{-1} = f^2 \cdot \mathrm{e}^{-2B(\sin\theta/\lambda)^2} \cdot \frac{1 + \cos^2 2\theta}{\sin^2\theta\cos\theta} \cdot A \tag{6}$$

where 2θ is the angle of the intermediate point of every angular interval $\Delta 2\theta$ and other symbols have the same meanings as those in equation (3).

Similarly to Kc_i, we define Ka as follows:

$$Ka = \frac{\sum_{2\theta = 2\theta_o}^{2\theta_p} C_{2\theta} \cdot Ia_{2\theta}}{\sum_{2\theta = 2\theta_o}^{2\theta_t} C_{2\theta} \cdot Ia_{2\theta}} \tag{7}$$

Then the total correction factor Fa for the amorphous components is given by

$$Fa = \bar{C}_p/Ka \tag{8}$$

Obviously the substantial crystallinity (Xcs) in semicrystalline component i in copolymers can be evaluated by the following equation:

$$Xcs = \frac{\sum_j^N Fc_{ij} \cdot Ic_{ij}}{\sum_j^N Fc_{ij} \cdot Ic_{ij} + Fa_i \cdot Ia_i} \times 100\% \tag{9}$$

RESULTS AND DISCUSSION

Characterization of the purified graft copolymers

The i.r. spectrum of the purified PS-g-PEO copolymer showed a characteristic peak at 1120 cm^{-1} for the C–O–C ether group, a peak at 2900 cm^{-1} for the methylene group, and two peaks at 1600 and 3050 cm^{-1} for the benzene rings. The i.r. spectrum of the purified P(BA–AA)-g-PEO copolymer showed a characteristic peak at 1120 cm^{-1} for the C–O–C ether group, a peak at 2920 cm^{-1} for the methylene group, two peaks at 3100 and 1710 cm^{-1} for the $-\mathrm{COOH}\cdots\overset{|}{\mathrm{O}}\mathrm{C_2H_4}-$ group, a peak at 1730 cm^{-1} for the carbonyl group, and a peak at 940 cm^{-1} for the butyl group.

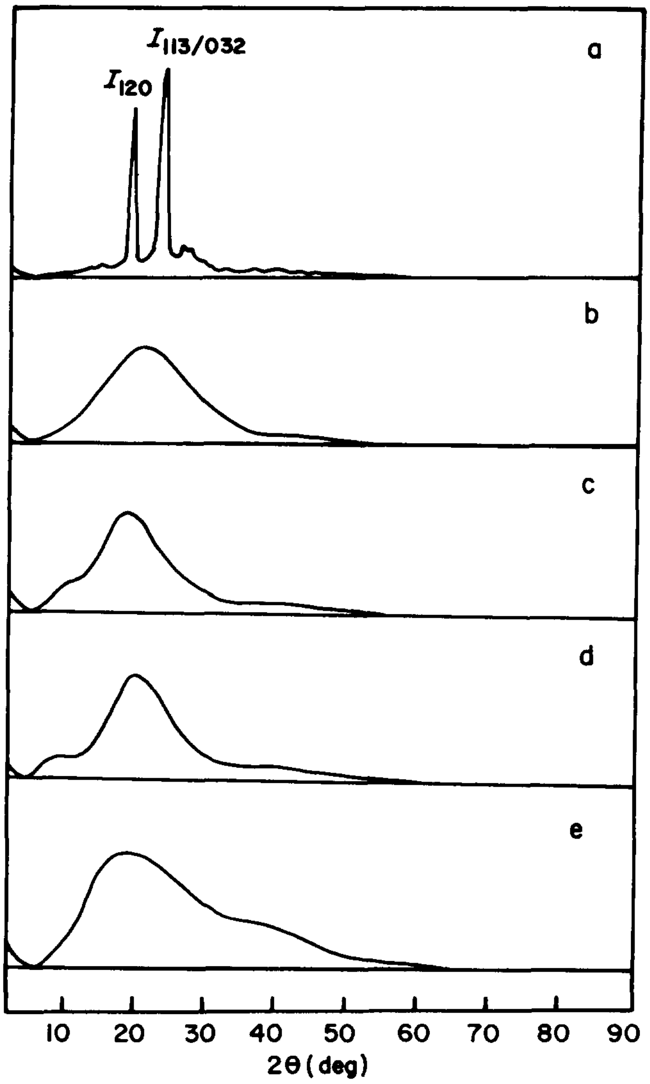

Figure 2 WAXS patterns of the homopolymers: (a) semicrystalline PEO; (b) amorphous PEO; (c) amorphous PS; (d) amorphous PBA; (e) amorphous PAA

The ^1H n.m.r. spectrum of the purified PS–g-PEO copolymer showed two peaks at 6.6–7.2 ppm from the phenyl ring protons, a peak at 3.7 ppm from the methylene group in $-CH_2CH_2O-$ units and a peak at 1.5 ppm from the $-CH(C_6H_5)CH_2-$ group. The ^1H n.m.r. spectrum of the purified P(BA–AA)-g-PEO copolymer showed a peak at 3.85 ppm from the butyl group, a peak at 3.5 ppm from the methylene group in $-CH_2CH_2O-$ units, and two peaks at 1.2 and 1.4 ppm from the $-\underset{|}{\overset{|}{C}}CH_3$ and $-CH_2-$ groups, respectively.

The i.r. and ^1H n.m.r. spectra of the purified copolymers demonstrated that they contained monomeric units of EO and S or EO, BA and AA.

WAXS patterns of the homopolymers and copolymers

The WAXS patterns of homopolymers PEO, PS, PBA and PAA are shown in *Figure 2*. It can be seen from this figure that there are about 22 peaks on the WAXS patterns of semicrystalline PEO; its two major crystalline peaks are at 19.1° and 23.3°. These two strong peaks correspond to 120 and 113/032 planes. On the other hand, all the scattering curves of amorphous PEO, PS, PBA and PAA are in the range 5° to 65°. There are several extreme values on each scattering curve and the slopes of the lines for separating background scattering are about -0.14 mm deg^{-1}. It is difficult and unnecessary to resolve the overlapping haloes from one another on WAXS patterns of the homopolymers.

Because the scattering intensity at a high 2θ angle of every component in the copolymers is obscured by background or is too weak to measure when the corresponding content in the copolymers is low, the WAXS patterns of the copolymers were scanned from 2° to 35° (*Figures 3* and *4*). It is obvious that the intensity of the crystalline peaks on the WAXS patterns is due to the contribution of the PEO component, whereas the intensity of the amorphous scattering curve is due to the contribution of PEO and PS or PEO, PBA and PAA. Thus the WAXS patterns for the copolymers must be resolved before the apparent crystallinity and substantial crystallinity can be evaluated.

The procedure for separating the background scattering and resolving between crystalline peaks and amorphous scattering curve is shown in *Figure 5*. It consists of the following steps. (1) Choose the angular range of measurement to be from 2° to 35°. (2) Select the lowest point M in the vicinity of 5°. (3) Draw a straight line with slope -0.14 mm deg^{-1} from M to N, separating the intensity components 'above' from the intensity components 'below'. (4) Select an intermediate point C in the vicinity of 21.2° at which the crystalline intensity is assumed to fall to zero (the separation between the two major crystalline peaks is 4.2°, which is regarded as

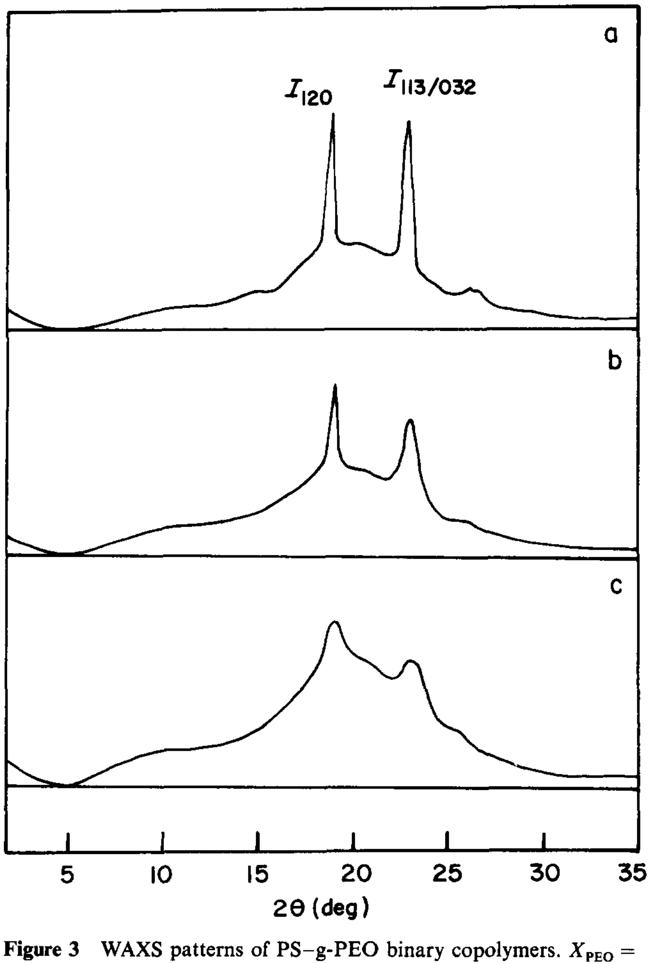

Figure 3 WAXS patterns of PS–g-PEO binary copolymers. X_{PEO} = (a) 41.5%; (b) 31.3%; (c) 23.4%

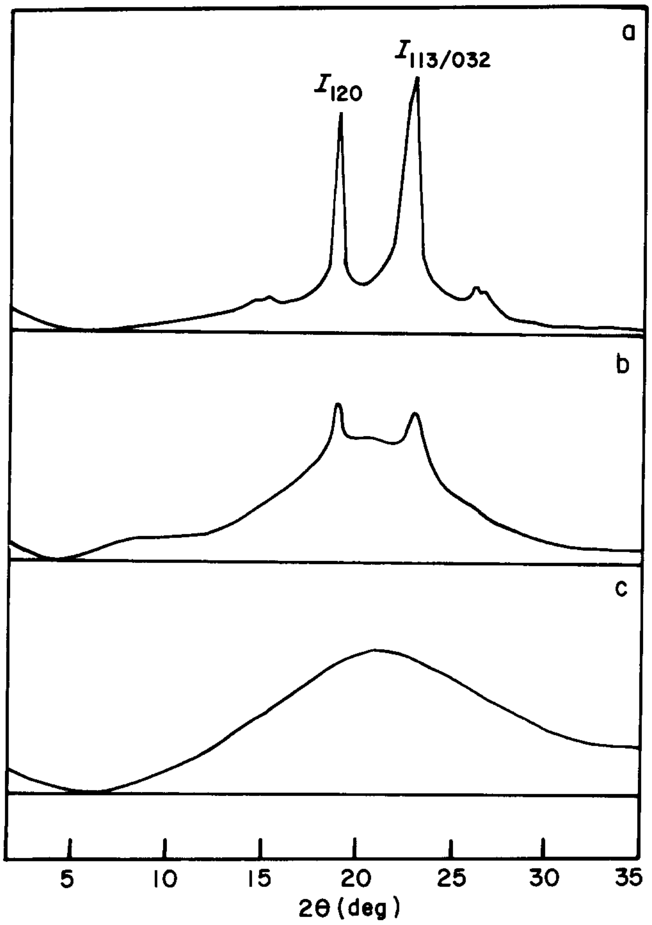

Figure 4 WAXS patterns of P(BA–AA)-g-PEO ternary copolymers: (a) $X_{PEO} = 70\%$, $X_{PBA.M} = 63\%$, $X_{PAA.M} = 37\%$; (b) $X_{PEO} = 36\%$, $X_{PBA.M} = 83\%$, $X_{PAA.M} = 17\%$; (c) $X_{PEO} = 32\%$, $X_{PBA.M} = 27\%$, $X_{PAA.M} = 73\%$

large enough to justify this assumption). (5) Select four points A(13°), B(16.5°), D(29.5°), and E(34°), at which the crystalline intensity falls to zero. (6) Draw a dashed line from point A to B, to C, to D, and to E, separating the crystalline intensity from the amorphous intensity.

The total area of the two strong peaks, I_{120} and $I_{113/032}$, above the line ABCDE is now taken to be proportional to the intensity of the major crystalline peaks of the PEO component. The area between the lines MABCDEN and MN, Ia_t, is taken to be proportional to the intensity of the overlapping scattering curve of the amorphous components.

Evaluation of Xca and Xcs in PS–g-PEO binary copolymers

According to equation (1) and *Figure 3*, the apparent crystallinity formula for PS–g-PEO copolymers can be written as follows:

$$Xca = \frac{F_{120}\cdot I_{120} + F_{113/032}\cdot I_{113/032}}{F_{120}\cdot I_{120} + F_{113/032}\cdot I_{113/032} + Fa_{PEO}\cdot Ia_{PEO} + Fa_{PS}\cdot Ia_{PS}} \times 100\% \quad (10)$$

Let $Ia_{PS} = 0$; then equation (10) becomes the substantial crystallinity formula for PEO grafts alone, namely

$$Xcs = \frac{F_{120}\cdot I_{120} + F_{113/032}\cdot I_{113/032}}{F_{120}\cdot I_{120} + F_{113/032}\cdot I_{113/032} + Fa\cdot Ia} \times 100\% \quad (11)$$

In order to separate the scattering intensity of amorphous PEO, Ia_{PEO}, from the total scattering intensity, Ia_t, equation (10) is divided by equation (11), giving

$$\frac{Xca}{Xcs} = \frac{F_{120}\cdot I_{120} + F_{113/032}\cdot I_{113/032} + Fa_{PEO}\cdot Ia_{PEO}}{F_{120}\cdot I_{120} + F_{113/032}\cdot I_{113/032} + Fa_{PEO}\cdot Ia_{PEO} + Fa_{PS}\cdot Ia_{PS}} \quad (12)$$

Substituting the content of PEO grafts, X_{PEO}, where $X_{PEO} = Xca/Xcs$, we have

$$X_{PEO} = \frac{F_{120}\cdot I_{120} + F_{113/032}\cdot I_{113/032} + Fa_{PEO}\cdot Ia_{PEO}}{F_{120}\cdot I_{120} + F_{113/032}\cdot I_{113/032} + Fa_{PEO}\cdot Ia_{PEO} + Fa_{PS}\cdot Ia_{PS}} \quad (13)$$

Solving equation (13), we obtain

$$Ia_{PEO} = \frac{X_{PEO}\cdot Fa_{PS}\cdot Ia_t - (1 - X_{PEO})(F_{120}\cdot I_{120} + F_{113/032}\cdot I_{113/032})}{X_{PEO}\cdot Fa_{PS} + (1 - X_{PEO})Fa_{PEO}} \quad (14)$$

Using equations (5) to (8) and setting $\Delta 2\theta = 2°$, the total correction factors for the scattering curves of amorphous PEO, PS, PBA and PAA were calculated. They are listed in *Table 1*. With the data in *Table 1* and the results $C_{120} = 1.00$, $C_{113/032} = 1.82$, and $Kc_{PEO} = 0.45$ for the two major crystalline peaks of semicrystalline

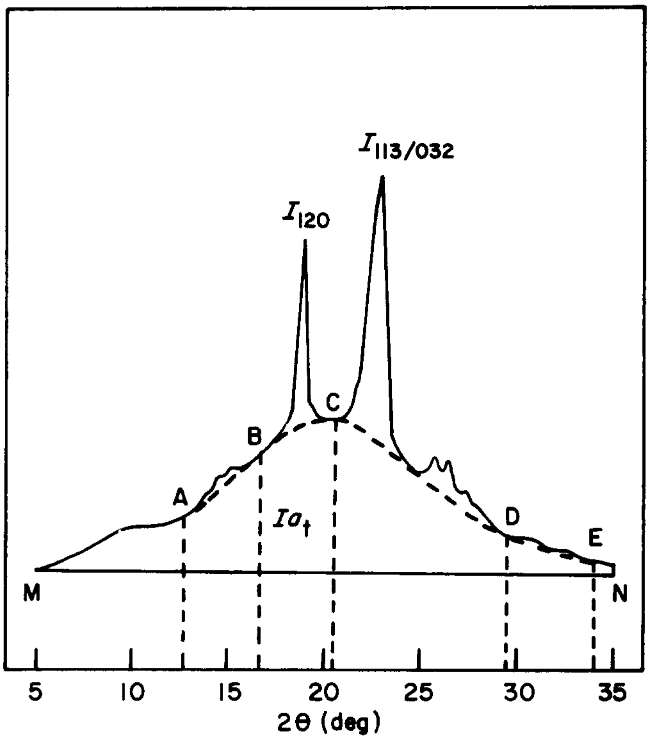

Figure 5 Procedure for separating the background scattering and resolution between crystalline peaks and amorphous curve. I_{120}, $I_{113/032}$ = relative integrated intensities of the major crystalline peaks of PEO graft chains; Ia_t = relative integrated intensity of the amorphous curve of the copolymer

Table 1 Total correction factors for amorphous PEO, PS, PBA and PAA

Homopolymer	$\sum_{2\theta=5^\circ}^{35^\circ} Ia_{2\theta}$	$\sum_{2\theta=5^\circ}^{35^\circ} C_{2\theta}\cdot Ia_{2\theta}$	$\sum_{2\theta=5^\circ}^{65^\circ} C_{2\theta}\cdot Ia_{2\theta}$	$\bar{C}_p$	Ka	Fa
PEO	26525	42410	72588	1.600	0.584	2.74
PS	37730	56584	157738	1.500	0.359	4.18
PBA	26435	39083	157423	1.478	0.248	5.96
PAA	27562	54468	189569	1.976	0.287	6.88

Table 2 Apparent and substantial crystallinity in PS–g-PEO copolymers

X_{PEO} (%)	$\bar{M}n_{PEO}$	I_{120}	$I_{113/032}$	Ia_t	Ia_{PEO}	Xca (%)	Xcs (%)
23.4	2200	1322	2403	105621	30428	3.1	13.2
28.0	2200	2644	4806	95888	29913	6.6	23.6
31.3	2200	3785	7570	79306	24125	11.6	37.1
35.2	2200	4806	10574	76302	23922	15.8	44.9
41.5	2200	6969	13818	60080	18730	24.1	58.1

PEO[11], equations (10), (11) and (14) can be further reduced to give

$$Xca = \frac{2.22I_{120} + 4.04I_{113/032}}{2.22I_{120} + 4.04I_{113/032} + 2.74Ia_{PEO} + 4.18Ia_{PS}} \times 100\% \qquad (15)$$

$$Xcs = \frac{2.22I_{120} + 4.04I_{113/032}}{2.22I_{120} + 4.04I_{113/032} + 2.74Ia} \times 100\% \qquad (16)$$

$$Ia_{PEO} = \frac{4.18X_{PEO}Ia_t - (1 - X_{PEO})(2.22I_{120} + 4.04I_{113/032})}{2.74 + 1.44X_{PEO}} \qquad (17)$$

After separation of the scattering intensity of the amorphous phase in the PEO grafts from the total amorphous scattering intensity using equation (17), the apparent crystallinity in PS–g-PEO copolymers and the substantial crystallinity in PEO grafts alone were calculated using equation (15) and equation (16), respectively. The results are listed in *Table 2*. It can be seen from this table that both *Xca* and *Xcs* increase with increasing PEO content or decrease with increasing PS content. The reason for the decrease of *Xca* is different from that for *Xcs*. The decrease of *Xca* is due to the increase of both the amorphous phase in PEO and amorphous PS. Even if the crystallization of the PEO grafts were not reduced by the PS backbone chains, *Xca* would still diminish because of the increase in PS content or the decrease in PEO content. So it is unlikely that *Xca* can distinctly characterize the change in crystallization of PEO grafts. On the other hand, the decrease of *Xcs* is due only to the increase in the amorphous phase in the PEO grafts. Hence *Xcs* can reveal the effect of PS backbone chains more distinctly and more reasonably than can *Xca*.

There is another example[11] to show the superiority of *Xcs*: when the Li^+/EO molar ratio is >0.33, *Xca* and *Xcs* in the complexes of PMMA–g-PEO with $LiClO_4$ decrease with increasing salt concentration. When $Li^+/EO = 0.25$, *Xca* is approximately equal to that in the corresponding copolymer, whereas *Xcs* is larger than that in the corresponding copolymer. So it can be understood that $LiClO_4$ can promote the crystallization of the PEO grafts when $Li^+/EO = 0.25$ by analysing the values of *Xcs* rather than those of *Xca*.

Evaluation of Xca and Xcs in P(BA–AA)–g-PEO ternary copolymers

For convenience, the amorphous phase in P(BA–AA)–g-PEO copolymers can be regarded as composed of amorphous PEO and a kind of matrix comprising amorphous PBA and PAA. In this way, the apparent crystallinity in P(BA–AA)–g-PEO copolymers can be written as follows:

$$Xca = \frac{2.22I_{120} + 4.04I_{113/032}}{2.22I_{120} + 4.04I_{113/032} + 2.74Ia_{PEO} + Fa_M\cdot Ia_M} \times 100\% \qquad (18)$$

where Fa_M is the total correction factor for the amorphous matrix, and Ia_M is the relative integrated intensity of the amorphous matrix.

Let $X_{PBA.M}$ and $X_{PAA.M}$ be the PBA content and PAA content of the matrix, respectively; then

$$\frac{X_{PBA.M}}{X_{PAA.M}} = \frac{Fa_{PBA}\cdot Ia_{PBA}}{Fa_{PAA}\cdot Ia_{PAA}} = \frac{Fa_{PBA}\cdot Ia_{PBA}}{Fa_{PAA}(Ia_M - Ia_{PBA})} \qquad (19)$$

Solving equation (19), we obtain

$$Ia_{PBA} = \frac{X_{PBA.M}\cdot Fa_{PAA}}{X_{PAA.M}\cdot Fa_{PBA} + X_{PBA.M}\cdot Fa_{PAA}}\cdot Ia_M \qquad (20)$$

Following the same procedure, we obtain

$$Ia_{PAA} = \frac{X_{PAA.M}\cdot Fa_{PBA}}{X_{PAA.M}\cdot Fa_{PBA} + X_{PBA.M}\cdot Fa_{PAA}}\cdot Ia_M \qquad (21)$$

Then we have

$$Fa_{PBA}\cdot Ia_{PBA} + Fa_{PAA}\cdot Ia_{PAA} = \frac{(X_{PBA.M}+X_{PAA.M})Fa_{PBA}\cdot Fa_{PAA}}{X_{PAA.M}\cdot Fa_{PBA} + X_{PBA.M}\cdot Fa_{PAA}}\cdot Ia_M \qquad (22)$$

Table 3 Total correction factors for the matrices

X_{PEO} (%)	$X_{PBA.M}$ (%)	$X_{PAA.M}$ (%)	$Fa_{PBA} \cdot Fa_{PAA}$	$X_{PAA.M} \cdot Fa_{PBA}$	$X_{PBA.M} \cdot Fa_{PAA}$	Fa_M
70	63	37	41.00	2.21	4.33	6.27
60	73	27	41.00	1.61	5.02	6.18
36	83	17	41.00	1.01	5.71	6.10
28	86	14	41.00	0.83	5.92	6.07
32	27	73	41.00	4.35	1.86	6.60

Table 4 Apparent and substantial crystallinity in P(BA–AA)–g-PEO copolymers

X_{PEO} (%)	$\bar{M}n_{PEO}$	I_{120}	$I_{113/032}$	Ia_t	Ia_{PEO}	Xca (%)	Xcs (%)
70	6000	6729	27036	43378	29387	42.5	60.7
60	6000	8652	18384	55274	34880	29.7	49.4
36	6000	2523	5768	98411	50033	6.3	17.4
28	7000	1202	2163	111989	49592	2.2	7.7
32	6000	0	0	146355	77758	0	0

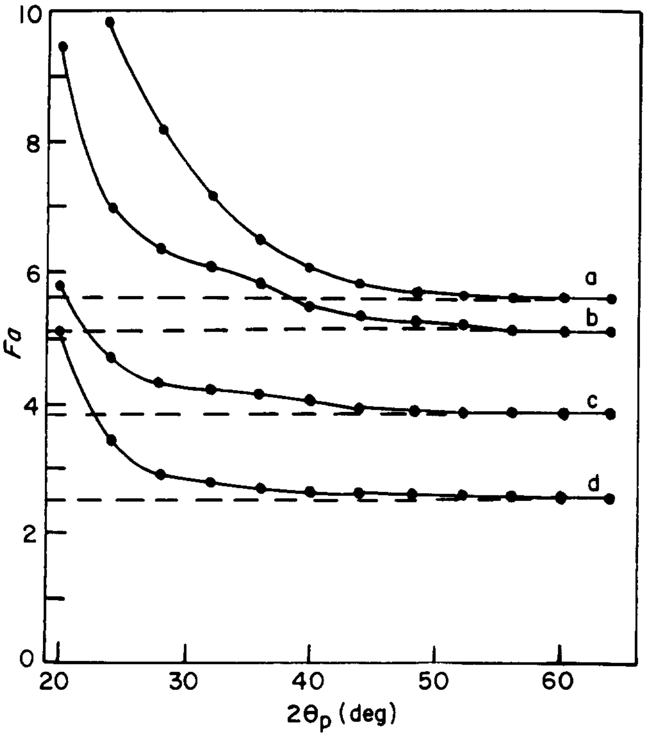

Figure 6 Total correction factor Fa as a function of $2\theta_p$: (a) amorphous PAA; (b) amorphous PBA; (c) amorphous PS; (d) amorphous PEO

Since

$$Fa_{PBA} \cdot Ia_{PBA} + Fa_{PAA} \cdot Ia_{PAA} = Fa_M \cdot Ia_M,$$

and $X_{PBA.M} + X_{PAA.M} = 1$, the total correction factor for the matrix is given by

$$Fa_M = \frac{Fa_{PBA} \cdot Fa_{PAA}}{X_{PAA.M} \cdot Fa_{PBA} + X_{PBA.M} \cdot Fa_{PAA}} \qquad (23)$$

When the scanning range and the types of amorphous homopolymers are fixed, the values of Fa for the amorphous homopolymers may be regarded as universal constants. Moreover, the chemical composition of the copolymer concerned is known in most cases. So Fa_M for the matrix can usually be calculated using equation (23).

For P(BA–AA)–g-PEO copolymers, the values of Fa_M for several samples of different chemical composition were calculated using equation (23). They are listed in *Table 3*.

With the data in *Table 3*, the apparent crystallinity in P(BA–AA)–g-PEO copolymers and the substantial crystallinity in the PEO grafts alone were calculated, as shown in *Table 4*. It can be seen from this table that both Xca and Xcs increase with increasing PEO content or decrease with increasing P(BA–AA) content, and the effect of PAA on the crystallization of the PEO grafts is greater than that of PBA. This second result may be due to the formation of hydrogen bonding between PEO and PAA[13].

Properties of the total correction factor

Obviously the total correction factor of the amorphous homopolymer is a function of scanning range. At a suitable value of $2\theta_p$, Fa_{PBA} would probably be equal to Fa_{PAA}, and we have $Fa_M = Fa_{PBA} = Fa_{PAA}$. In this case, Fa_M is not affected by the chemical composition of the matrix. *Figure 6* shows that the curve of Fa for PBA does not cross that for PAA. This means that there is no suitable value of $2\theta_p$ at which Fa_{PBA} is equal to Fa_{PAA}. It can also be seen from *Figure 6* that each Fa has a limit value when $2\theta_p$ is large enough. A smaller limit value of Fa means that more scattering intensity of the amorphous homopolymer is distributed over a lower 2θ angle (see *Figure 2*).

In order to demonstrate the universal property of Fa, two types of amorphous polymer were examined. One was synthesized with BA and EA (ethyl acrylate), the other was made up of one half of a PBA slab and one half of a PEA slab. The PBA contents of the two samples were approximately 50%. Scanning of the two samples showed that they had approximately the same curve shapes. Hence it is thought that the total correction factor Fa can be used to correct the amorphous scattering intensity of copolymers.

CONCLUSIONS

The total correction factor obtained by profile analysis of amorphous homopolymers can be used to correct and resolve the overlapping amorphous curves of binary and ternary copolymers. This method is quite general, because most amorphous polymers are not usually orientated.

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