Structural changes in the grafted copolymer polyethylene–styrene

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The general method for phase analysis was used on X-ray diffractograms of copolymers produced by the direct and the indirect method of grafting styrene to polyethylene. It was established that both copolymer systems show small deviations from a two-phase structure. Up to a polyethylene to polystyrene ratio of 1:1 the grafting process did not cause any substantial change in crystalline structure. Crystallites were not destroyed in either system. The main structural changes resulting from grafting appeared in disordered regions of polyethylene. The diffraction curves determined for individual structural states are discussed and used as a basis to construct structural models.

INTRODUCTION

Although the effect of structural characteristics of polyethylene on the grafting reaction and resulting copolymer structure have been investigated, structural changes arising from grafting have not yet been fully defined$^{1-6}$. Different authors have reached contradictory conclusions regarding the final structure of the grafted copolymer$^{1-6}$ especially with relation to changes in crystallite organization and those occuring within crystallites. Different experimental conditions may be one reason for such disagreements. Even less is known about changes in disordered regions of polyethylene.

To establish the type and extent of structural changes occuring with increasing radiation dose, and thus with increasing polystyrene content, X-ray diffraction analysis was used. Wide angle diffractograms indicate a decrease in crystallinity, i.e. an increase in the proportion of disordered regions, as a result of the grafting process. In spite of some contradictory conclusions$^{1-3}$, quantitative estimates of these changes led to the proposal that no crystal destruction occurs at relatively low grafting yields^{2,3}. However, the specific features of the diffractograms of copolymers did not permit more definite conclusions to be drawn about more subtle structural changes occuring during grafting. In order that these questions might be resolved, diffractograms of copolymer samples were subjected to the general method of phase analysis (GMPA), which allows determination of the number and nature of phases present in multiphase systems^{7}.

THEORETICAL

The use of GMPA on X-ray diffractograms of complex multicomponent systems^{7} allows determination of: (1) number of phases in the system; (2) nature of these phases; (3) quatitation of their proportions.

The number of phases in a given system is determined by correlating diffraction curves, i.e. the sum functions $\Phi_i(x)$ represented by Fourier coefficients $F_i(n)$. For the $(r+1)$th sample of an r-phase system, the criterion for the number of phases is given by the equation:

$$\sum_{i=1}^{r} \alpha_i F_i(n) = F_{r+1}(n) \tag{1}$$

where $F_i(n)$ are Fourier coefficients representing the i-th diffraction curve $\Phi_i(x)$; n = number of Fourier coefficients; α_i = coefficients of proportionality calculated from a large number of equations (1) by the method of least squares. The deviations $\Delta(n)$ of coefficients of the Fourier series $F_{r+1}(n)$ calculated using equation (1), from experimental values for $F_{r+1}(n)$ manifest themselves in the magnitude of the deviation factor R_f and in the following statistical parameters: correlation factor R and Student's parameter t_i.

The deviation factor R_f is defined by:

$$R_f = \frac{\sum_n |\Delta(n)|}{\sum_n |F_{r+1}(n)|} \tag{2}$$

When the proposed number of phases is correct, the deviation factor R_f is sufficiently small.

A quantitative determination of phases in a system requires knowledge of the exact shapes of diffraction curves for the relevant phases, i.e. individual functions $\Phi_i(x)$. The theory of GMPA allows individual functions $\varphi_i(x)$ to be represented in the form:

$$\varphi_i(x) = \sum_{j=1}^{r} \varepsilon_{i,j} \Phi_j(x) \tag{3}$$

The transformation factors $\varepsilon_{i,j}$ which are used in equation (3) are related to the weight fractions, $w_{i,j}$, by the inverse matrix:

$$\begin{pmatrix} w_{1,1} & \cdots & w_{1,r} \\ \vdots & & \vdots \\ w_{r,1} & \cdots & w_{r,r} \end{pmatrix} \cdot \begin{pmatrix} \varepsilon_{1,1} & \cdots & \varepsilon_{1,r} \\ \vdots & & \vdots \\ \varepsilon_{r,1} & \cdots & \varepsilon_{r,r} \end{pmatrix} = \mathrm{I} \tag{4}$$

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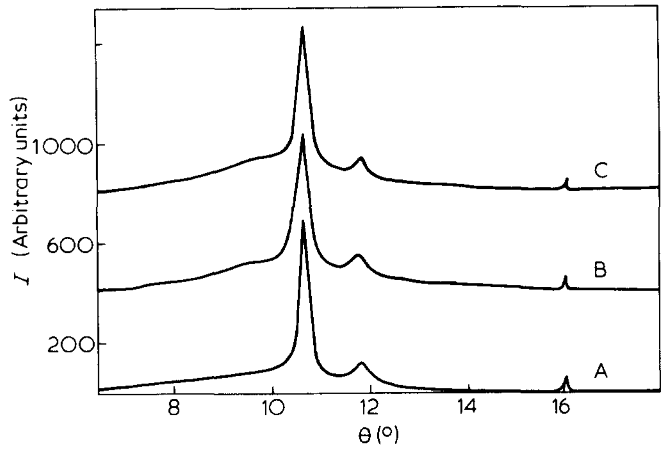

Figure 1 Diffractograms of polyethylene (A) and grafted copolymers I with a PS yield of 53.7% (B) and 102.0% (C)

Individual functions $\varphi_i(x)$ can be easily calculated from equation (3) if the transformation factors $\varepsilon_{i,j}$ are determined, i.e. if the weight fractions, $w_{i,j}$, are known. When the weight fractions of the phases are not known, approximations of $\varepsilon_{i,j}$ can be made which can then be used to determine the most probable individual functions. However, in practice it was found that shapes of similar diffraction curves for two amorphous states had to be determined and that some differences in the shape of discrete diffraction maxima of crystallites were important. For these reasons the use of logical conditions did not give staisfactory results[6]. A solution to the problem of diffuse diffraction curves of amorphous states has been found[8] and is applied in this paper.

When only one amorphous phase is present in the system, individual functions of this phase $\varphi_A(x)$ may be calculated by correlating the sum functions[8]. The calculation of individual functions is based on the fact that the Fourier series of such a smooth curve converges more rapidly than that representing discrete diffraction maxima of the crystalline phase. For this reason the number, $2k$, of Fourier coefficients which has to be calculated for the determination of a smooth curve is usually less than the total number, $2n$, of equations of the system:

$$\sum_{i=1}^{r-1} \alpha_i \Phi_i(x) + \varphi_A(x) = \Phi_{r+1}(x) \qquad (5)$$

therefore the calculation uses the method of least squares. The calculated function $\varphi_A(x)$ is an exact fit for the diffraction curve of an amorphous phase if only one such phase is present in the system. However, if two or more amorphous structural states are present in the system then the calculated function $\varphi_A(x)$ represents a linear combination of the diffraction curves of respective amorphous phases. Therefore in such a case it is most convenient to calculate the function $\Delta(x)$ by correlating approximate shapes of individual amorphous phase functions. This function is then used to correct the hypothetical diffraction curves of the amorphous phases.

In a concrete case one starts from individual functions of crystalline $\varphi_K(x)$ and amorphous phase $\varphi_{PE}(x)$ of polyethylene, and amorphous polystyrene $\varphi_{PS}(x)$[9] which are then correlated with the sum function of each sample:

$$\sum_{i=1}^{3} \alpha_i \varphi_i(x) + \Delta(x) = \Phi_j(x) \qquad (6)$$

The $\Delta(x)$ function is used to correct the shapes of diffraction curves for the amorphous phases of PE and PS. $2k$ Fourier coefficients, which represent the $\Delta(x)$ function, are calculated simultaneously with the proportionality coefficients by the method of least squares if the condition $2k+3 \ll 2n$ is satisfied. When this is not the case, Fourier coefficients are calculated pair by pair.

Using the calculated individual functions $\varphi_i(x)$, the fractions of various phases within the system can be quantitatively determined[7]:

$$\sum_{i=1}^{r} \alpha_i f_i(n) = F_j(n) \qquad (7)$$

where $f_i(n)$ is the Fourier series of the i-th individual function and $F_j(n)$ is the Fourier series of the sum functions of the j-th sample.

EXPERIMENTAL

Grafting of styrene onto polyethylene was carried out in a vacuum of 10^{-5} mmHg, with γ-radiation at 3000 rad h^{-1} and 40°C using the direct (I) or the indirect (II) method[10].

The polyethylene used for grafting was a low density LUPOLEN prepared as a film (70 × 7 mm) of 0.2 mm thickness and freed of additives. The styrene monomer had been previously distilled.

After grafting, samples were extracted with benzene, washed and weighed. The yield of polystyrene, P_g, was calculated, for both series, from the increase in sample weight.

Copolymer samples from both series, as well as polyethylene and polystyrene, were scanned on a reflection diffractometer with CuK$_\alpha$ radiation in the range of $\theta = 4$ to 23°. *Figure 1* shows diffractograms for selected copolymers I.

For the calculation procedure eight samples with a polystyrene yield $P_g = 0$ to ~100% were taken from each series (*Table 1*). The range of Bragg angles, θ, between 7 and 15 degrees, was used for calculation because the most intense diffuse diffraction maxima of polyethylene and polystyrene, as well as the discrete diffraction maxima 110 and 200, was found here.

After separating off incoherent radiation, the interval between 7 and 15 degrees was divided into 160 equal parts at which points the intensities were measured. Diffraction intensities in the whole interval were corrected for absorption, i.e. brought to a constant diffracting mass[11]. A UNIVAC 1100 computer was used to normalize the intensities; calculate the Fourier series for relevant curves and the criterial parameters from equations (1) and (2);

Table 1 Total grafting yields

	Polystyrene yields, (P_g %)	
Sample	Copolymers I	Copolymers II
1	0.0	0.0
2	32.7	26.0
3	43.0	41.3
4	53.7	50.7
5	60.8	66.0
6	71.8	71.2
7	86.8	91.5
8	102.0	109.2

Table 2 Deviation factors R_f and factors of correlation $|R|$ for correlated sum functions $\phi_j(x)$ of copolymers I and II

	Copolymers I		Copolymers II	
Combination	R_f	$\|R\|$	R_f	$\|R\|$
1 2 5	0.094	0.998	0.143	0.996
1 2 7	0.132	0.996	0.190	0.992
1 3 5	0.076	0.998	0.106	0.998
1 4 7	0.184	0.991	0.151	0.994
1 6 7	0.032	1.000	0.049	0.998
2 4 6	0.119	0.996	0.089	0.998
2 5 7	0.081	0.998	0.085	0.999
2 5 8	0.112	0.997	0.129	0.997
3 5 8	0.111	0.997	0.133	0.997
4 5 6	0.057	0.999	0.035	1.000
1 2 4 8	0.076	0.999	0.159	0.994
1 3 5 6	0.032	1.000	0.032	1.000
1 3 5 8	0.064	0.999	0.080	0.999
2 3 4 7	0.110	0.997	0.128	0.996
2 3 5 7	0.081	0.999	0.080	0.999
2 3 5 8	0.108	0.997	0.123	0.997
2 4 6 8	0.131	0.996	0.089	0.998
1 2 3 5 7	0.046	1.000	0.056	0.999
1 3 4 5 6	0.031	1.000	0.032	1.000
1 2 3 5 8	0.041	1.000	0.076	0.999
2 3 5 6 7	0.033	1.000	0.050	0.999
3 4 5 6 7	0.034	1.000	0.058	0.999
1 2 3 5 6 8	0.040	1.000	0.064	0.999

determine shapes of diffraction curves for individual structural states and determine their quantitative fraction in the sample.

RESULTS

The criterial equation (1) was used to determine the number of microphases present in copolymers I and II. Assuming a two-phase nature for the system, correlation was performed within sets of three diffraction curves represented by 80 cos and 80 sin Fourier coefficients. The statistical parameter R and the deviation factor were calculated (*Table 2*). The values of the deviation factor R_f for copolymers I were in the range $R_f = 0.032$–0.184, and the correlation factors were $R = 0.991$–1.000. Theoretically R_f has to be zero, but it is usually in the range $0 < R_f \leqslant 0.05$ because of experimental errors. Although the values of the correlation factor are high it is not possible to confirm the hypothesis of copolymer I having two phases since the condition $R_f \leqslant 0.050$ is not fully satisfied. Because of similarities between diffractograms of some consecutive samples, certain combinations of these correlated curves do give a value of $R_f \leqslant 0.050$. Correlation of four sum curves gives smaller values of $R_f = 0.032$–0.131, whereas a correlation of five or more sum curves fully satisfies the criterial condition ($R_f \leqslant 0.050$). The deviation factor is not large when three sum functions are correlated, therefore it may be considered that when GMPA is applied to diffractograms of copolymer I, small deviations from a two-phase system are detected. However, the fact that the criterial conditions is strictly satisfied when five sum curves are correlated points towards the system being four-phase.

In the case of copolymer II the values of the R_f factor falls continually in series: three correlated sum curves ($R_f = 0.035$–0.190), four curves ($R_f = 0.032$–0.159), five curves ($R_f = 0.032$–0.138), six curves ($R_f = 0.047$–0.077) and seven correlated curves ($R_f = 0.040$–0.053) (*Table 2*). The decrease in R_f is gradual, attributed to a better fit of the equations with a large number of terms. The detected deviations from a two-phase system appear to be small. The criterial condition is not satisfied even when a greater number of curves are correlated. We assume therefore, that at least one structural component changes from sample to sample, thus introducing into the system an undefined number of phases.

Most probable shapes of curves relating to individual structural states were determined by calculating the $\Delta_j(x)$ function while correlating individual functions $\varphi_K(x)$, $\varphi_{PE}(x)$ and $\varphi_{PS}(x)$ with the sum functions $\Phi_j(x)$ using, equation (6). The $\Delta_j(x)$ functions of copolymer I and II, which are obtained by calculating 30 sin and 30 cos coefficients, are shown in *Figures 2* and *3* respectively. On the basis of these curves corrections were made to the shape of the discrete diffraction maxima 110 and 200 of polyethylene, i.e. the curves of $\varphi_K(x)$ for each sample. *Figure 4* shows corrected diffraction curves $\varphi_K(x)$ of copolymer I and *Figure 5* those of copolymer II.

The change in ratio of relative intensities of the diffraction maxima 110 and 200 was small but systematic for copolymer I. For all samples of copolymer grafted by the direct method the position of discrete maxima 110 and 200 on corrected curves did not indicate any change in unit cell dimensions.

No systematic change in the ratio I_{110}:I_{200} was observed in copolymers obtained by the indirect method. However, the change in position of diffraction maxima indicates a change in unit cell dimensions: a_0 increases from 7.508 Å (PE) to 7.571 Å (sample with 109.2%

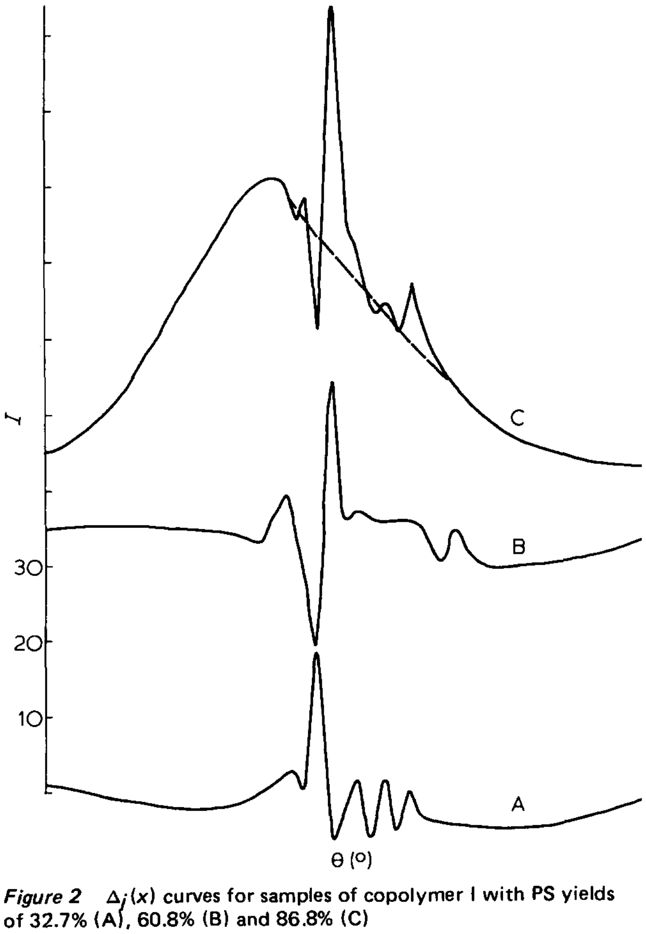

Figure 2 $\Delta_j(x)$ curves for samples of copolymer I with PS yields of 32.7% (A), 60.8% (B) and 86.8% (C)

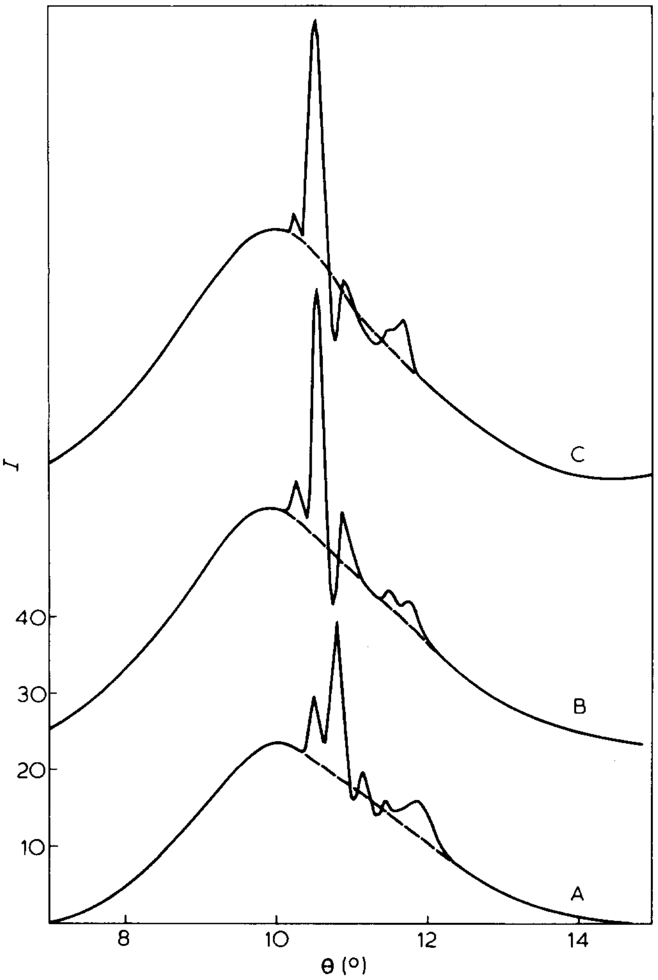

Figure 3 $\Delta_j(x)$ curves for samples of copolymer II with PS yields of 26.0% (A), 66.0% (B) and 91.5% (C)

polystyrene yield) and b_0 from 4.983 Å (PE) to 4.998 Å (sample with 109.2% polystyrene yield).

The corrected shapes of discrete diffraction maxima $\varphi'_K(x)$ were used to calculate the smooth functions $\Delta_j(x)$ using equation (6), this time defined by only 10 sin and 10 cos Fourier coefficients. $\Delta_j(x)$ curves of copolymer I become more prominent only with an increased polystyrene yield, whereas those of copolymer II are already relatively large in the sample with lowest yield of polystyrene (26%). The suplementary functions $\Delta_j(x)$ were correlated amongst themselves in order to establish their nature. The results of such a correlation lead to the conclusion that there are smaller differences in the shape of $\Delta_j(x)$ curves for copolymer I than for copolymer II and consequently it cannot be established with certainty whether they have a one- or two-component character. In the case of copolymer II the results confirm the two-component nature of the $\Delta_j(x)$ curve.

Taking into account the two-component nature of the $\Delta_j(x)$ function of copolymer II, and assuming likewise for copolymer I, it is necessary to determine which part of the $\Delta_j(x)$ function relates to the correction of diffraction curves for the amorphous phase of polyethylene $\varphi_{PE}(x)$, and to the correction for polystyrene $\varphi_{PS}(x)$. After such corrections the individual curves obtained $\varphi'_{PE}(x)$ and $\varphi'_{PS}(x)$ were normalized, and quantitative fractions of the relevant components were determined. *Figure 6* shows some corrected curves $\varphi'_{PE}(x)$, and *Figure 7* some corrected curves $\varphi'_{PS}(x)$ of copolymer I, compared with the original diffraction curves $\varphi_{PE}(x)$ and $\varphi_{PS}(x)$. The maximum in $\varphi_{PE}(x)$ shows practically no change in position, while the systematic shifts of $\varphi'_{PS}(x)$ correspond to a change (by Bragg's equation) of the d-value from 4.40 to 4.50 Å (for sample with 102.0% PS yields).

Figures 8 and *9* show curves $\varphi'_{PE}(x)$ and $\varphi'_{PS}(x)$ respectively of copolymer II. The diffraction maximum of the amorphous phase of PE (*Figure 8*) shifts towards greater angles and this corresponds to a change in d-value of 4.48 Å (PE) to 4.38 Å (sample with 109.2% PS yield), while the shift of the main diffraction maximum of polystyrene corresponds to a change in average d from 4.41 Å (sample with 26.0% PS yield) to 4.70 Å (sample with 109.2% PS yield).

DISCUSSION

Visual comparison of diffractograms of copolymers produced by the direct and indirect method did not indicate any decomposition or reorientation of crystallites, nor any change in unit cell dimensions. These results agree with previously published conclusions[2,3]. However this does not rule out the possibility of some minor changes in the degree of perfection of crystallites, and their reorganization within complex morphological forms[4,5]. More subtle changes of specific components in a complex copolymer system could be discerned by using GMPA on diffractograms of the copolymer. A small systematic change in relative intensities of the maxima 110 and 200 in

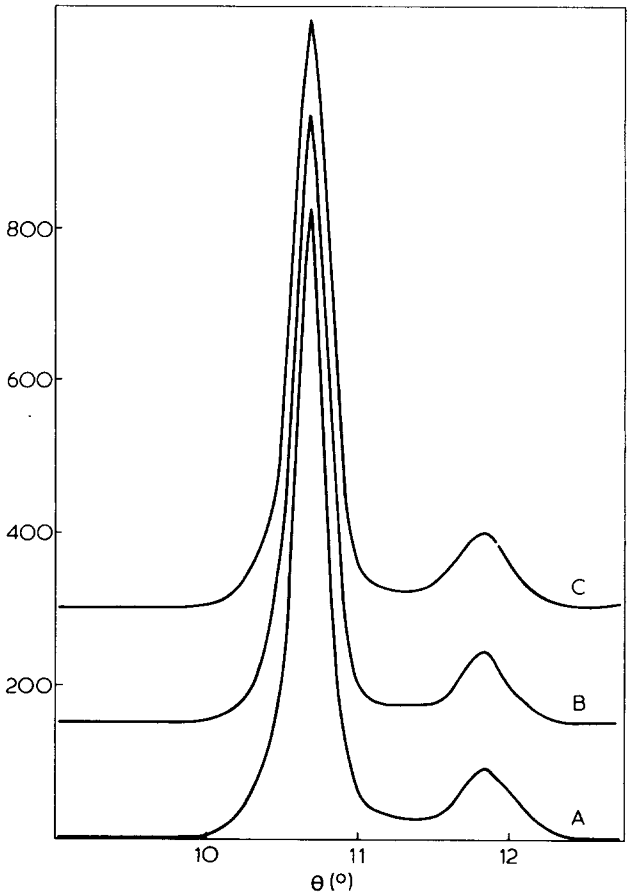

Figure 4 Individual curves of the crystalline phase of PE (A) and samples of copolymer I with PS yields of 43.0% (B) and 102.0% (C)

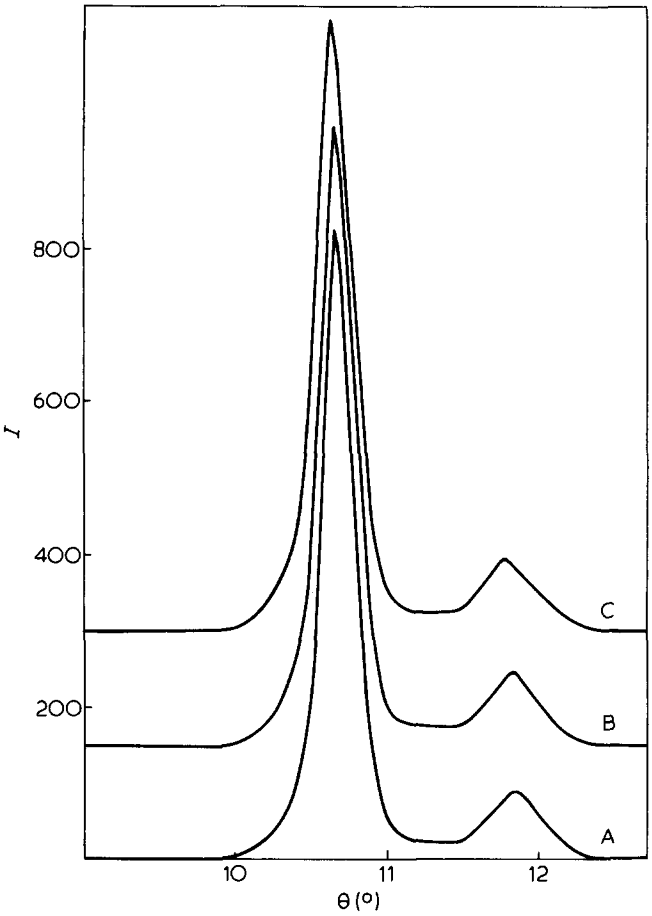

Figure 5 Individual curves of the crystalline phase of PE (A) and samples of copolymer II with PS yields of 26.0% (B) and 109.2% (C)

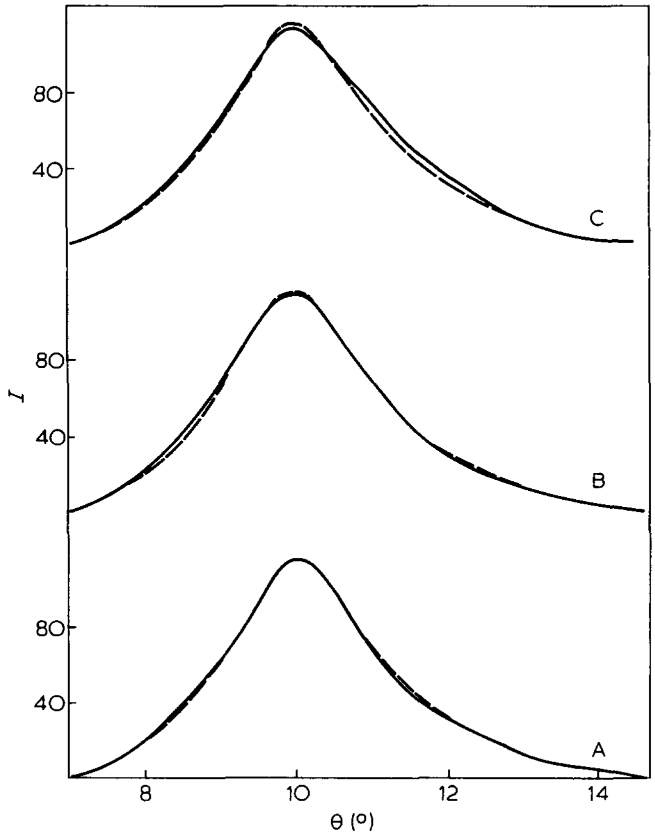

Figure 6 Calculated curves $\phi'_{PE}(x)$, (——), for samples of copolymer I with PS yields of 53.7% (A), 71.8% (B), and 102.0% (C) compared with $\phi_{PE}(x)$, (— — —)

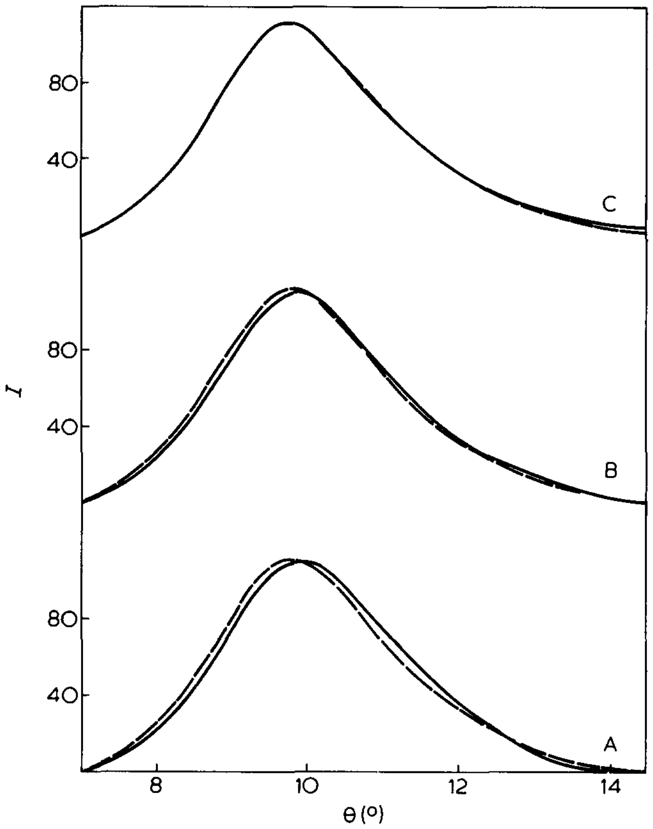

Figure 7 Calculated curves $\phi'_{PE}(x)$, (——) for samples of copolymer I with PS yields of 53.7% (A), 86.8% (B) and 102.0% (C) compared with the diffractogram of PS (— — —)

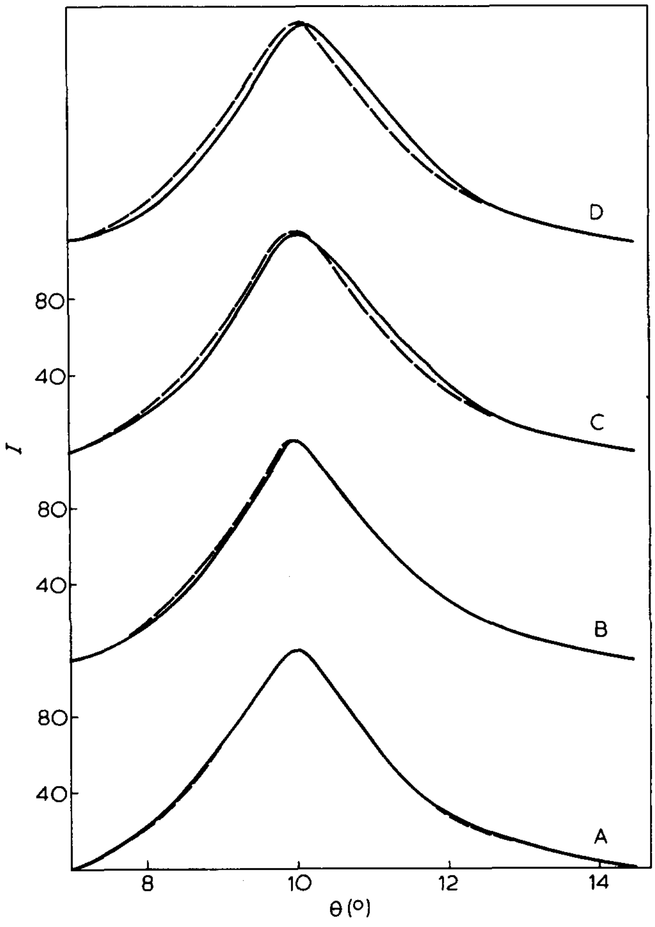

Figure 8 Calculated curves $\phi'_{PE}(x)$, (——), of copolymer II with PS yields of 26.0% (A), 41.3% (B), 66.0% (C) and 91.4% (D) compared with 91.5%, (— — —)

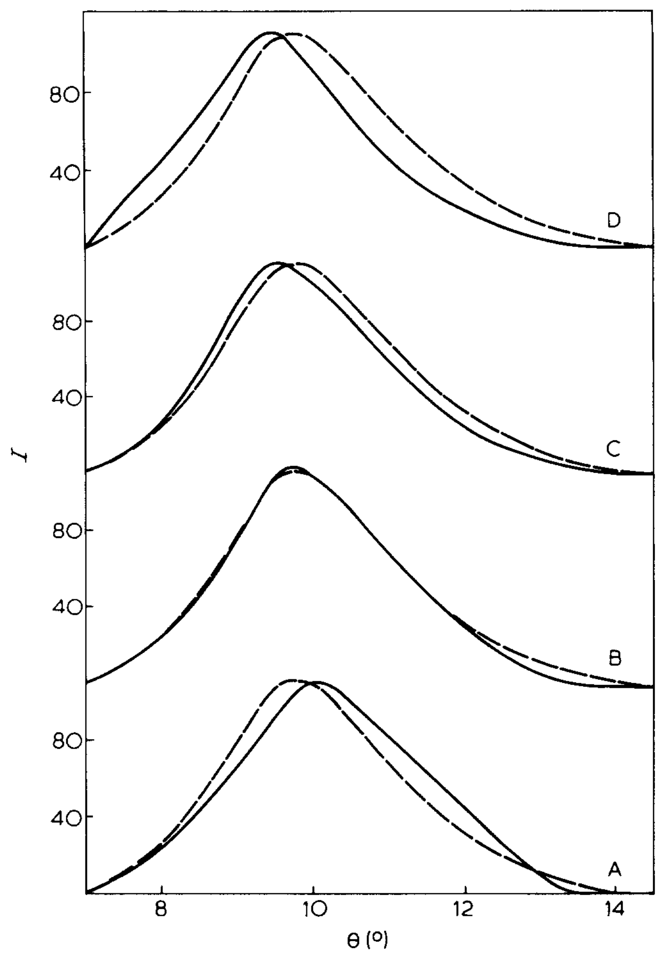

Figure 9 Calculated curves $\phi_{\hat{P}S}(x)$, (——), of copolymer II with PS yields of 26.0% (A), 50.7% (B), 71.2% (C) and 91.5% (D) compared with the diffractogram for PS (– – –)

copolymers obtained by the direct method indicates a change in crystallite orientation. Presumably the pressure exerted by expanding regions, primarily of polystyrene homopolymer, is sufficient to break the loose, lateral, intercrystalline links. Furthermore the small systematic change in unit cell dimensions which follows grafting of styrene to pre-irradiated polyethylene leads to the conclusion that grafting of polystyrene macromolecules increases the imperfection of the crystallite surface and indirectly influences the increase in average unit cell dimensions. The effect is similar to that of an increase in branch content[12], or of chlorination of PE[13]. This explanation fits the hypothesis that grafting by the indirect method occurs primarily at the crystallite surface.

The greatest structural changes take place in disordered regions of polyethylene. The results of determining shapes of individual curves for separate structural components do not agree with results expected from a mixture of polyethylene and polystyrene. In the case of the direct grafting method there is practically no change in the crystalline microphase, and changes in the disordered region of PE are barely noticeable. The incorporated polystyrene microphase shows somewhat greater changes than that of PE. Therefore the copolymer would seem to resemble an incompatible mixture of PE and PS components in which the changeable polystyrene component is dispersed in the polyethylene film in the form of small packets. According to this model, the copolymer would consist of three different structural states. However some of the correlation results point to the possibility that the polystyrene microphase is not uniform. The polystyrene microphase of copolymer I changes less than that of copolymer II, when the total polystyrene yield is the same, which may indicate that only a small part of the polystyrene component changes. Such a hypothesis would assume the existence of a separate region, structurally comparable to the polystyrene homopolymer. A smaller fraction of the polystyrene component would be liable to structural change. Probably polystyrene chains, grafted into interlamellar or lateral intercrystalline regions, form microdomains which differ structurally from the larger domains of polystyrene homopolymer (*Figure 10*). Thus three amorphous, structurally recognizable states would exist: the first similar to amorphous polyethylene; the second similar to amorphous polystyrene homopolymer; and the third consisting of domains, predominantly of grafted PS chains. The system would therefore contain four components.

The results show that the supplementary function $\Delta_j(x)$ changes from sample to sample of copolymer II, i.e. they suggest the conclusion that the disordered regions change qualitatively during grafting. The two component nature of the supplementary functions, and the systematic changes in diffraction curves of amorphous PE and amorphous PS with increasing PS yield lead to the conclusion

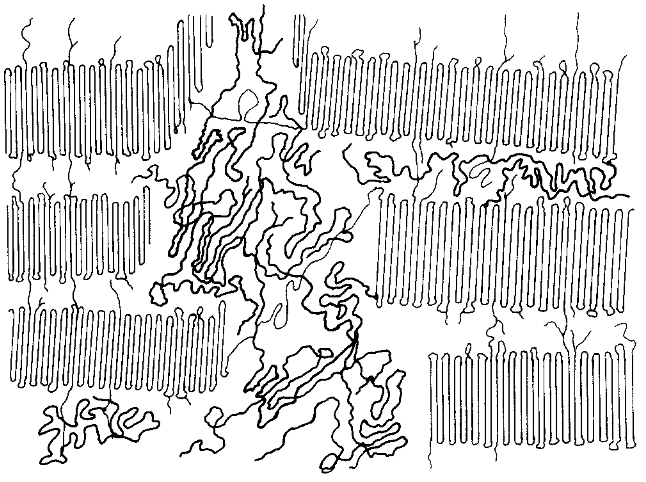

Figure 10 Schematic drawing of the structure of copolymer I

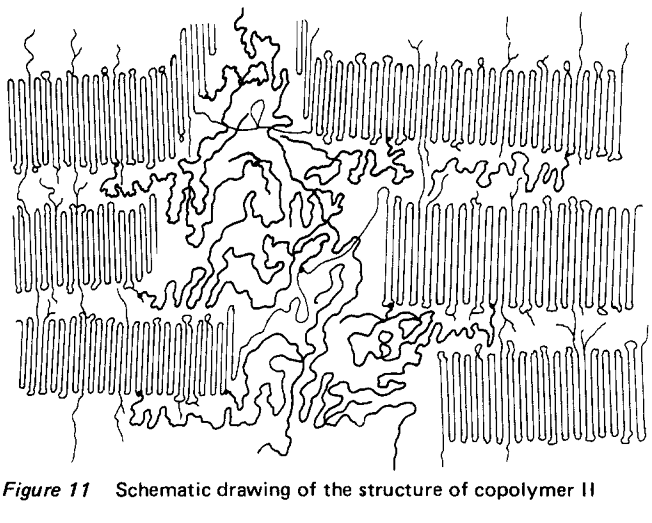

Figure 11 Schematic drawing of the structure of copolymer II

that alongside the crystalline microphase there exist two disordered microphases of a changeable nature. One microphase, similar to amorphous polyethylene is liable to slight change, but only at high grafting yields. The other, similar to polystyrene, changes more noticeably during grafting. This could be explained by the assumption that, with relatively small radiation doses, styrene chiefly grafts into microfissures of polyethylene, through which it diffuses. The microfissures widen and styrene enters into lateral intercrystalline regions of relatively low density. While being grafted onto the crystallite surface, macromolecules of PS disrupt the subsurface layer of the crystallite and increase average unit cell dimensions. In this way polystyrene chains push apart the flexible polyethylene chains and thus initiate a slight but continuous change in the diffraction pattern of amorphous PE showing that interchain spacing is decreased (*Figure 11*). This change may perhaps linked to crosslinking of mobile PE segments. The diffraction pattern of polystyrene shows a more pronounced increase in average interchain spacing. An analogous effect has been noticed on heating[14] and irradiating[15] polystyrene. This may be linked with conformational changes in grafted polystyrene macromolecules.

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