On the analysis of wide-angle X-ray diffraction curves of poly(vinyl chloride) samples

Saul J. Guerrero* and Hector Veloso
Intevep SA, Seccion de Petroquimica, Apartado Postal 76343, Caracas 1070-A, Venezuela

and Ernani Randon
Departamento de Electronica y Circuitos, Universidad Simon Bolivar,
Apartado Postal 80659, Caracas, Venezuela
(*Received 30 August 1988; revised 25 September 1989; accepted 13 November 1989*)

The calculation of crystallinity values based on wide-angle X-ray diffraction (WAXD) curves of poly(vinyl chloride) (PVC) is subject to three conditions, which are not always explicitly stated. First, the sample should have no orientation or else an averaging factor must be applied to the intensity data. Secondly, on subtracting the non-crystalline component from the WAXD profile the resulting crystalline curve must conform to some identifiable unit cell. Thirdly, the potential presence of a mesomorphous phase implies that there may be no unique non-crystalline profile applicable to all PVC WAXD curves. This last condition is highlighted through the use of a Fourier-transform filtering function, which can be applied to separate the amorphous contribution from the overall WAXD profile. While this technique has been found to be applicable to a wide variety of semicrystalline polymer WAXD profiles, it consistently fails in the case of commercial PVC WAXD curves. The presence of a variable mesomorphous phase can alter the expected intensity relation between the 2 0 0 and 1 1 0 reflections, thus interfering in any straightforward crystallinity calculation based on WAXD profiles.

(Keywords: poly(vinyl chloride); wide-angle X-ray diffraction; crystallinity; Fourier filters)

INTRODUCTION

Early papers on plasticized poly(vinyl chloride) (PVC) mentioned the existence of discrete diffraction rings on wide-angle X-ray diffraction (WAXD) transmission photographs[1,2]. In 1956 Natta and Corradini[3] identified the unit cell as orthorhombic, with dimensions $a = 10.6$ Å, $b = 5.4$ Å and $c = 5.1$ Å. On the basis of the quality of the diffraction patterns, they concluded that along the c axis there is less development of order than along the other two axes[3]. In 1959 Fordham, Burleigh and Sturm[4] reported that decreasing the polymerization temperature increased the syndiotacticity, and thus the crystallinity of PVC. In 1960 a very crystalline, but very insoluble, PVC was obtained by White[5] on irradiating vinyl chloride as a urea canal complex. Burleigh[6] in 1960 and Rosen, Burleigh and Gillespie[7] in 1961 reported the synthesis of a very crystalline low-molecular-weight PVC by polymerizing the monomer in the presence of aldehydes.

In 1973 Wilkes, Folt and Krimm[8], on the basis of measurements carried out on this type of PVC, refined the parameters of the orthorhombic unit cell to $a = 10.24$ Å, $b = 5.24$ Å and $c = 5.08$ Å. The crystallizing potential of either commercial or low-temperature polymerized PVC was further demonstrated by reports published in 1979–80 regarding the existence of two crystal populations, each with a different thermal and orientation behaviour in dried PVC gels[9,10].

Parallel to studies of crystalline structures in PVC are reports concerning the existence of a mesomorphous phase in the polymer. Mammi and Nardi[11] in 1963 assigned the presence of a broad maximum at $d = 5.4$ Å to the existence of a mesomorphous fraction. Later work published by Lebedev *et al.*[12], Baker, Maddams and Preedy[13], Gilbert and Vyvoda[14] and Biais *et al.*[15] has all contributed further evidence for the existence of this phase. Guerrero, Meader and Keller[16] published the WAXD profile measured at 180°C of commercial PVC and concluded that it has a major contribution from the mesomorphous component in PVC.

The need to assign crystallinity values for PVC samples has led to the adoption of 'amorphous' backgrounds, which are fitted in different ways to the experimental curves[17–26]. It is sometimes accepted that values calculated in this manner have only a relative significance at best. This paper will analyse which conditions should be met by any curve-fitting procedure used to arrive at crystallinity values and will present some new approaches to the problem.

EXPERIMENTAL

Sample preparation

Experimental details on the preparation of samples have been given elsewhere[27,28]. PVC samples correspond to commercial suspension and microdispersion grades manufactured by Pequiven (Venezuela) under the tradenames Petroplas PP 140 and PP 330. The synthesis of the low-molecular-weight PVC aldehyde is described in ref. 29.

X-ray diffraction equipment and conditions of measurement

Details are given in ref. 27.

---

* To whom correspondence should be addressed at: Pequiven SA, Division de Nuevos Desarrollos, Apartado 2066, Caracas, Venezuela

0032-3861/90/091615-08

Data handling and computation

Programs were written in BASIC and run on microcomputers (IBM XT or Apple Macintosh). The fast Fourier algorithm[30] was used to obtain the Fourier transform where necessary.

RESULTS

Figure 1 indicates the WAXD profile that could be expected from a crystalline fraction in PVC. Peak positions and areas have been calculated on the basis of the accepted orthorhombic unit cell, according to the values reported in ref. 16.

Therefore, when it comes to choosing a general method for calculating crystallinity from WAXD profiles, it could be argued that, whatever amorphous profile is used or chosen, on subtraction from the WAXD profile of the sample the resulting curve should bear some similarity to *Figure 1*, taking into account possible broadenings of the reflections due to small crystallite size.

This is usually not the case. First of all, not all PVC samples give the same general WAXD profile. Samples can be classified into three types of profile based on the relative intensities of the 2 0 0 and 1 1 0 reflections.

Type A. The 2 0 0 reflection is clearly less intense than the 1 1 0 reflection. Two examples are a PVC aldehyde sample (*Figure 2*) and a well annealed plasticized commercial-grade PVC (*Figure 3*).

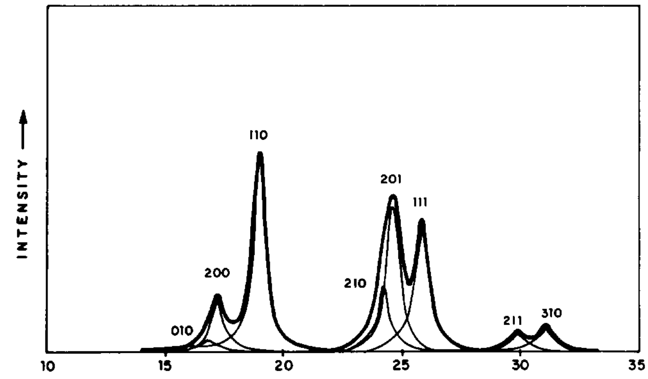

Figure 1 Example of crystalline peak profile to be expected from an orthorhombic unit cell for PVC, according to ref. 16. Peak shapes are assumed to be Lorentzian

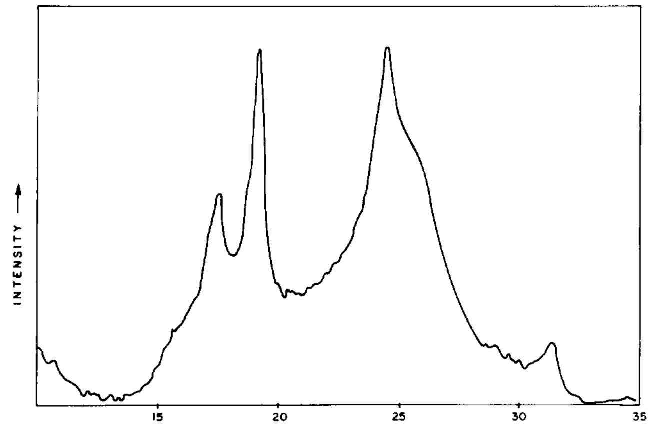

Figure 2 WAXD profile, after correcting baseline slope, of PVC aldehyde sample

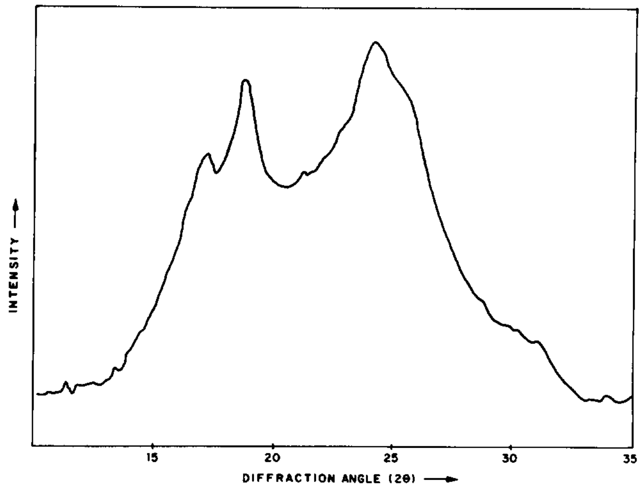

Figure 3 WAXD profile, after correcting baseline slope, of a plasticized PVC sample (80 pph dioctyl phthalate), annealed at 110°C for 3 h. Sample was extracted in diethyl ether prior to measurement

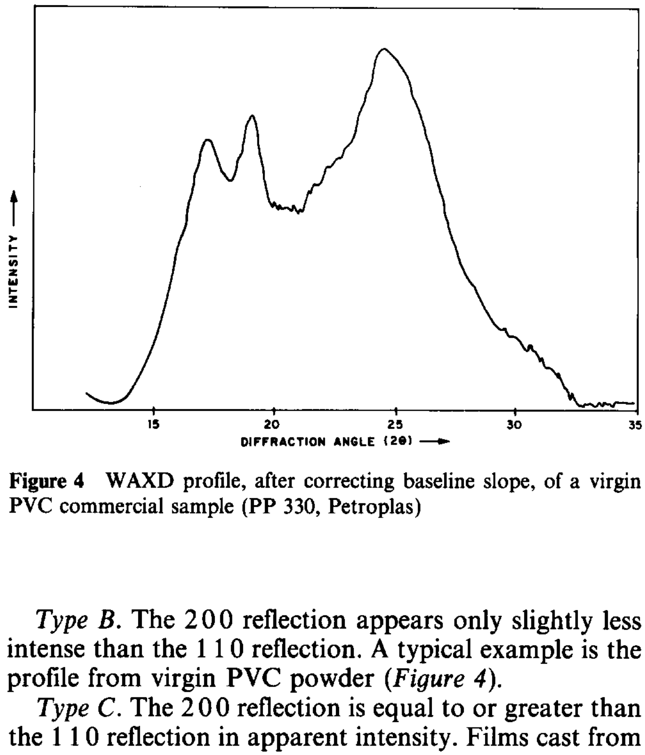

Figure 4 WAXD profile, after correcting baseline slope, of a virgin PVC commercial sample (PP 330, Petroplas)

Type B. The 2 0 0 reflection appears only slightly less intense than the 1 1 0 reflection. A typical example is the profile from virgin PVC powder (*Figure 4*).

Type C. The 2 0 0 reflection is equal to or greater than the 1 1 0 reflection in apparent intensity. Films cast from solvents give patterns such as *Figure 5*. Hot-pressed films can give even greater changes in the relative peak intensities (*Figure 6*). If these samples are immersed in diethyl ether for a period of hours, then the patterns revert to type B (*Figure 7*).

Obviously, sample preparation prior to measurement is determining the type of profile observed. The differences can be ascribed to one or more of the following causes:

(1) There are modifications in the unit cell of PVC.

(2) The samples present orientation.

(3) The mesomorphous content varies according to sample preparation.

The first explanation has already been explored by Vickers[31] some years ago, the basic argument being that the 1 1 0 reflection is specially sensitive (more than the 2 0 0) to small rotations of the molecules along their long axis, so that the WAXD profile can be altered through imperfections in the crystallizing units.

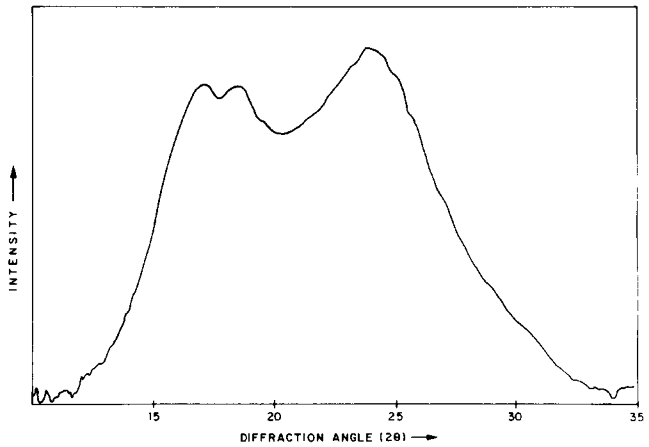

Figure 5 WAXD profile, after correcting baseline slope, of a commercial suspension-grade PVC (PP 140, Petroplas) cast from tetrahydrofuran

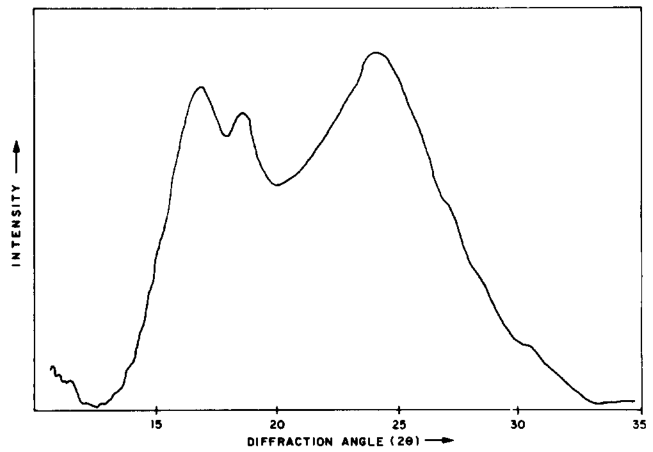

Figure 6 WAXD profile, after correcting baseline slope, of a commercial suspension-grade PVC (PP 140, Petroplas) after hot pressing

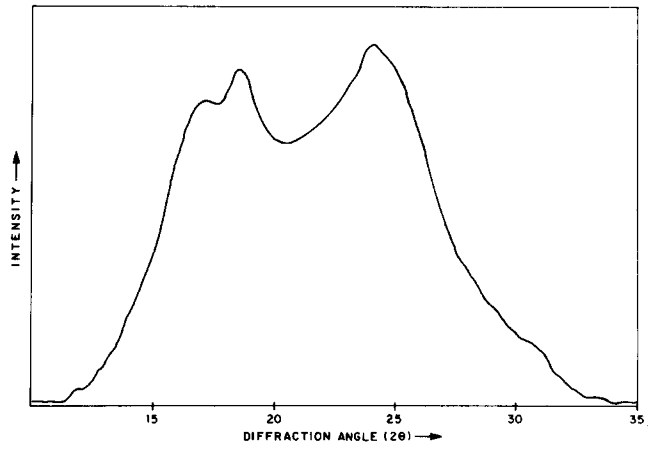

Figure 7 WAXD profile, after correcting baseline slope, of the sample from *Figure 7*, but after immersion overnight in diethyl ether

The second explanation has been known to apply to hot-pressed gel films[10], where planar orientation of the crystals enhances the 200 reflection in photographs taken with the beam perpendicular to the film plane. In the present instance the profiles corresponding to type C change on immersion in diethyl ether. Pole figures of samples after immersion show virtually no orientation[27] so that an initial conclusion would be that the ether relaxes the strains in the film and eliminates residual orientation. Thus, profiles such as type C indicate orientation of the sample in the film plane, and therefore are not suitable for crystallinity calculations.

Since a type B profile does not change after immersion of the sample in diethyl ether, the difference between it and a type A profile must have a different explanation. If an orthorhombic unit cell is held to be valid, then it is necessary to invoke a variable mesomorphous phase to try to explain a type B profile. The reason is straightforward. If the usually reported type 1 amorphous profile is subtracted from a type B curve, the 200 and 110 reflections remain of nearly equal intensity. The only way to obtain an intensity relationship between the 200 and 110 reflections near the expected value is by subtracting an 'amorphous' profile with a maximum at $2\theta = 17°$ of higher intensity than is usually reported. As stated in a previous study[16], this is indicative of a mesomorphous fraction present in the structure.

If these premises are valid, then the immediate implication is that there is no one, universal non-crystalline diffraction profile for PVC, but rather a variable profile according to the prior history of the sample. The pictorial summary of *Figure 8* includes two types of amorphous profile: type 1 corresponds to the widely used profile and type 2 is a WAXD profile measured at 180°C and assumed to represent a certain fraction of mesomorphous phase in the structure[16]. Curve-fitting procedures have shown that in practice a type B WAXD profile can yield a crystalline profile analogous to *Figure 1* by subtracting a combination of type 1 and type 2 amorphous backgrounds (see *Figure 9*).

The conclusion that there must be a mesomorphous phase that influences the profile of WAXD patterns of commercial PVC samples is also arrived at from a completely different line of approach to the problem of determining consistent crystalllinity values for PVC samples. This new approach involves the use of Fourier-transform filtering functions, and shows a potential application beyond the scope of the present subject matter.

In the field of electronics, filters are commonly employed on the Fourier-transform functions to eliminate sections of the frequency spectrum that contain unwanted information. An extension of this application is the elimination of noise (high-frequency signals) from instrumental spectra[32]. In the case of the analysis of WAXD profiles to arrive at crystallinity indices, the object of using a filter would be to separate, with as little distortion as possible, the broad signals associated with the amorphous phase from the narrower signals due to the crystalline phase. It should be clear at this point that the proposed use of Fourier-transform techniques is totally unrelated to the more standard application of this mathematical tool in the field of crystallography. The interest behind the present approach is to use the actual experimental data to self-generate, with as little bias as possible, the most consistent profile for the amorphous WAXD scatter. In the case of polymers such as PVC, where there are no readily available ways of generating suitable amorphous samples in the laboratory, the potential applications of such a method are worth exploring.

Figure 10 illustrates the basis of the proposed method. On the left-hand side are drawn the hypothetical (but probable) WAXD profiles of 100% crystalline (top) and

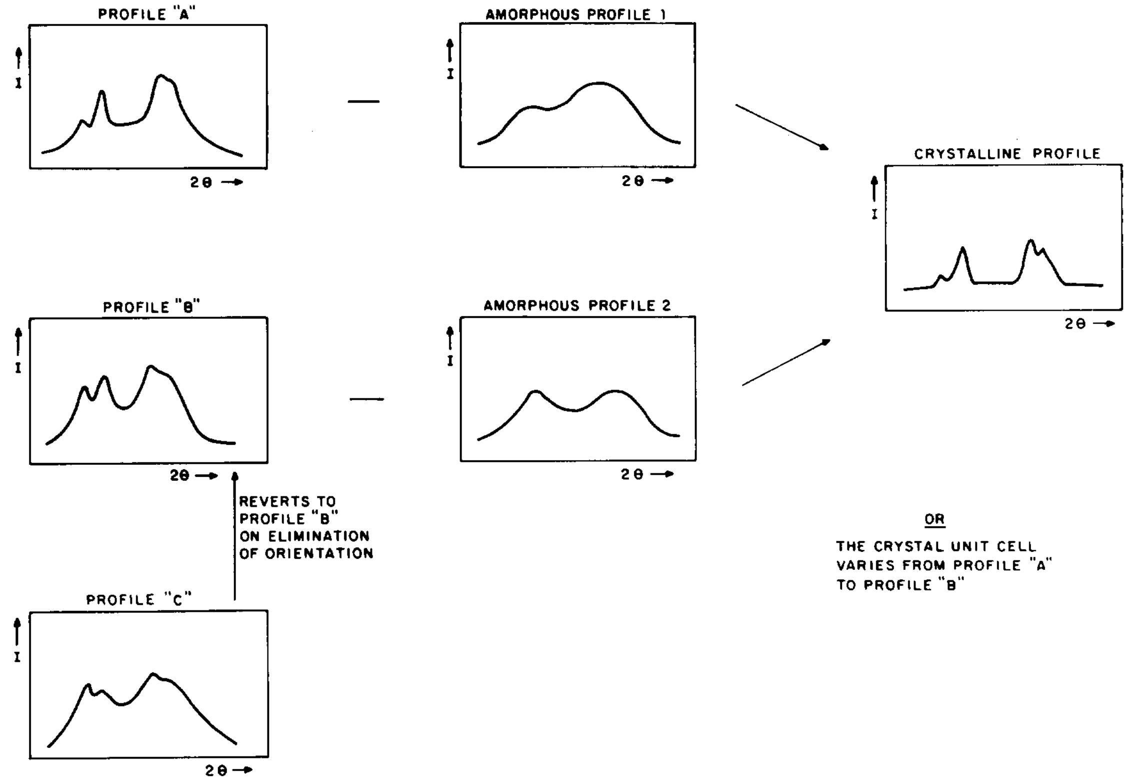

Figure 8 Pictorial summary of the possible correlations and necessary interrelations between WAXD profiles of PVC and proposed amorphous profiles

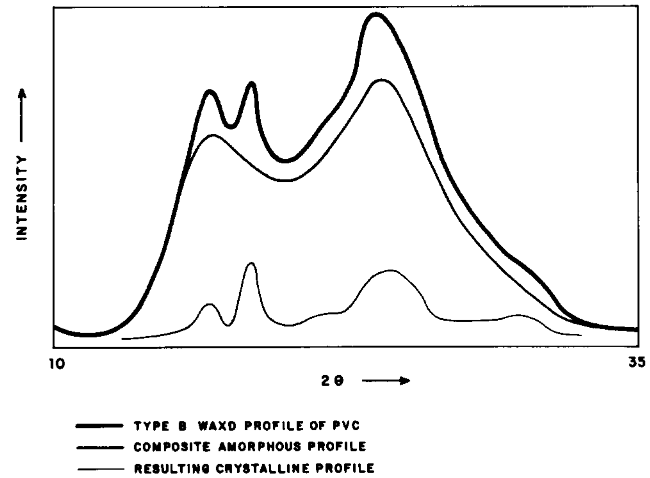

Figure 9 Manual curve fitting of a non-crystalline amorphous profile (composite type 1 and type 2) to a type B WAXD pattern. This fit has been carried out simply to illustrate how the intensity ratio between the 2 0 0 and 1 1 0 reflections can be approximated to the expected value

100% amorphous (bottom) PVC samples. The method assumes that each WAXD profile can be treated simply as a signal that repeats itself in time. To avoid unwanted distortion effects, this requires a correction of the baseline offset in the experimental data, so that the intensity values at the limiting measuring angles (in the present case $2\theta = 10°$ and 35°) have the same value. Using the fast Fourier-transform algorithm, 250 terms of the Fourier-transform series should in theory be generated. However, in practice, only 125 terms are generated, since the remainder constitute a mirror image of the first. Generally the sub-index for each term can be related in frequency to the time interval at which data are measured in the original signal. Even though in the present case that correlation is not strictly applicable, the higher sub-indices of the terms will be referred to as the high-frequency end of the spectrum.

Observing *Figure 10* it can be seen that though the amorphous profile has a Fourier transform limited to the low-frequency range, the transform of the crystalline profile extends over the low- and high-frequency range values. Therefore, a low-pass filter applied to a composite signal will produce a spectrum with a majority component contributed by the amorphous fraction. The choice of filter will evidently determine the degree of distortion introduced by this method, and thus the quality of the final information. One way of choosing the filter is to find a function that resembles as closely as possible the shape of the Fourier transform of the amorphous WAXD profile. However, since the purpose of the exercise is to work with samples where this profile is unknown, the type of filter applied in the present example is one which will suppress the high-frequency end of the spectrum while trying to minimize the low-frequency loss of information. One such low-pass filter is represented by the following function:

$$h(i)=\begin{cases} 1 & \text{for } i=0 \\ \dfrac{\sin(i\pi/M)}{(i\pi/M)} & \text{for } 1<i\leqslant M \\ 0 & \text{for } M<i\leqslant N \text{ data} \end{cases}$$

The method has been found to give good results with WAXD profiles generated by different polymer samples. This is illustrated in *Figures 11* to *13*. *Figure 11* corresponds to a polyethylene sample. A small shift to the lower 2θ values is applied to the filtered (amorphous) signal in order to optimize the result on subtracting it

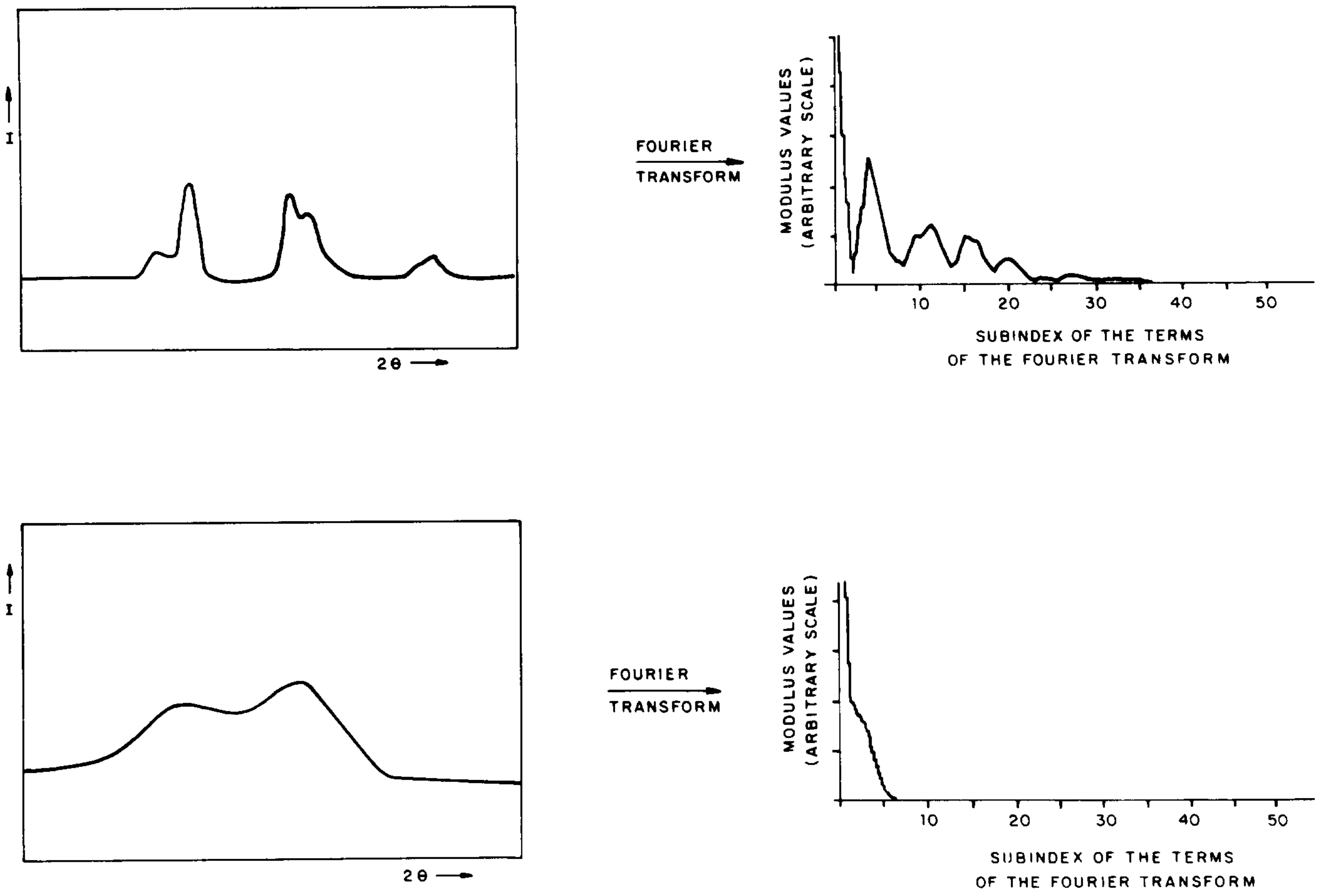

Figure 10 Fourier-transform modulus *versus* Fourier series index of a crystalline (top) and amorphous (bottom) WAXD profile of PVC

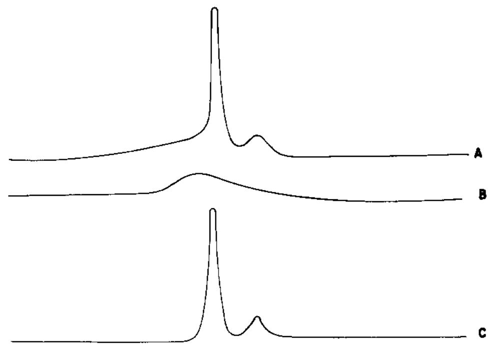

Figure 11 (A) WAXD profile of low-density polyethylene. (B) 'Amorphous' profile generated by filtering A, after manual shift. (C) 'Crystalline' profile obtained by subtracting B from A

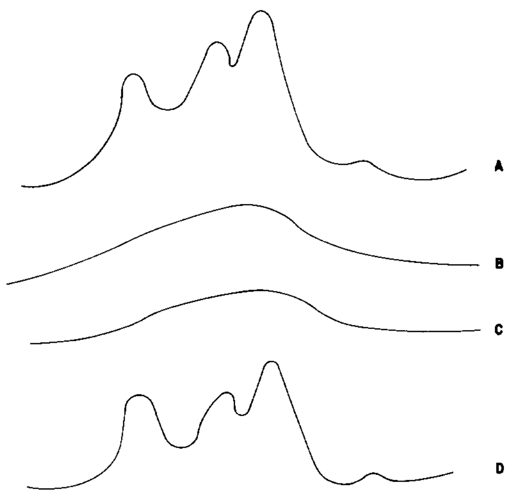

Figure 12 (A) WAXD profile of poly(ethylene terephthalate). (B) 'Amorphous' profile generated by filtering A. (C) Experimental amorphous profile. (D) 'Crystalline' profile obtained by subtracting B from A, virtually identical to curve obtained by subtracting C from A

from the original signal. With less crystalline patterns, such as illustrated in *Figure 12* (poly(ethylene terephthalate)), a very good correspondence is also achieved between the filtered amorphous profile and the experimentally measured WAXD amorphous profile. In this case no shift was applied to the filtered signal.

The need to shift the filtered curves arises from the fact that the filter used in the present examples allows part of the signal from the crystalline peaks to influence the resulting (filtered) amorphous profile. In some cases the presence of a sharp and strong crystalline reflection will influence unevenly the resulting amorphous profile, thus making it impossible simply to shift the filtered curve in order to optimize the fit. Such a situation is shown in *Figure 13*, and corresponds to a polystyrene sample. A visual comparison of the experimental amorphous curve and the 'amorphous' curve obtained after filtering shows the displacement of the latter towards the position of each of the main crystalline peaks. In this example the resulting 'crystalline' profile is obviously affected by the imperfect fit of the filtered amorphous profile with respect to the original signal, in spite of any manual shifting applied to optimize the result.

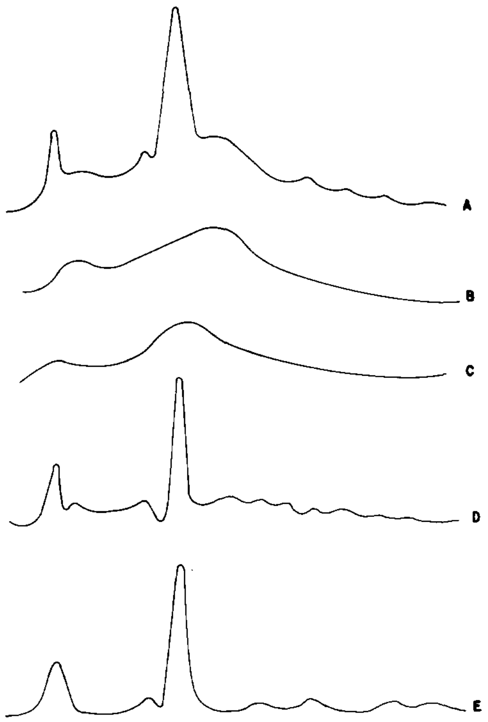

Figure 13 (A) WAXD profile of isotactic polystyrene. (B) Experimental amorphous profile. (C) 'Amorphous' profile generated by filtering A. (D) 'Crystalline' profile obtained by subtracting C from A. (E) 'Crystalline' profile obtained by subtracting B from A

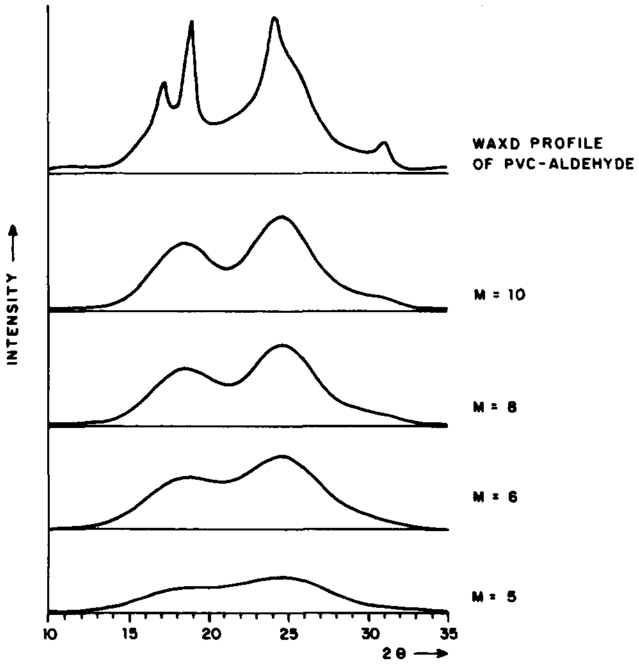

Figure 14 Filtered function of the WAXD profile of PVC aldehyde, using different values of M in the low-pass filter function (see text)

Overall, the examples show the following points:

(1) The profile of the generated 'amorphous' curve closely follows that of the known experimental amorphous WAXD profiles.

(2) The type of filter used in this paper cannot eliminate the influence of the crystalline phase on the final shape of the amorphous maxima. Manual shifting of the filtered function can certainly optimize the fit and thus validate to a high degree the resulting 'crystalline' profile.

(3) In spite of the apparent limitation of the previous point, the results obtained by applying this technique show clearly the shape and position of the crystalline peaks. Any contamination of the signal due to the shift in the filtered 'amorphous' profile has not been observed to influence the relative intensity of the crystalline peaks to any great extent.

Having applied the method to polymer samples where it is possible to measure experimentally the WAXD profile of an amorphous specimen, and bearing in mind the limitations of the method, the technique was subsequently applied to PVC WAXD profiles.

To start with, the filter was applied to the more crystalline WAXD pattern corresponding to a PVC aldehyde low-molecular-weight sample. *Figure 14* shows the various types of amorphous backgrounds that are generated according to the value of M (the cut-off point included in the filter function). If these profiles are subtracted from the original WAXD profile, after carrying out a scaling down to avoid negative values, then results such as those of *Figure 15* are obtained.

The overall shape of the profiles in *Figure 15* corresponds to the theoretical profile of *Figure 1*, with exceptions as to the apparent displacement of the 0 1 0 reflection closer to the 2θ value as reported by Natta and Corradini[3] and the broader 1 1 1 reflection. The value of M obviously determines the crystallinity index calculated for the sample. While $M=5$ cuts off a sizeable part of the amorphous contribution, values of $M=6$ to 8 give a reasonable indication that crystallinity is in the 36 to 40% range. For this particular sample, $M=6$ gives the profile with less distortion in the 20 to 23° (2θ) range. Similar profiles such as *Figure 2*, constructed artificially and of 'known' crystallinity, also give a good correlation for $M=6$. However, it must be stressed that the value for M will vary according to the polymer sample.

Figure 16 corresponds to the results obtained when the same filter is applied to a type B WAXD profile. The

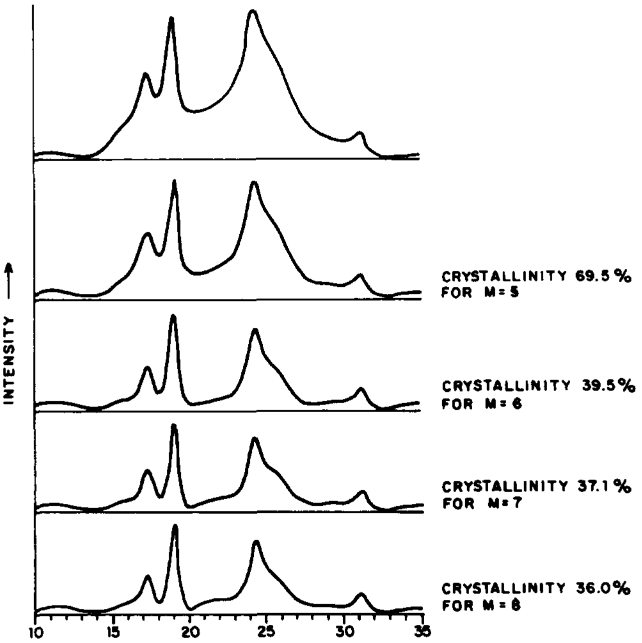

Figure 15 Crystalline profiles obtained after subtracting filtered functions shown in *Figure 14* from the original WAXD profile of PVC aldehyde

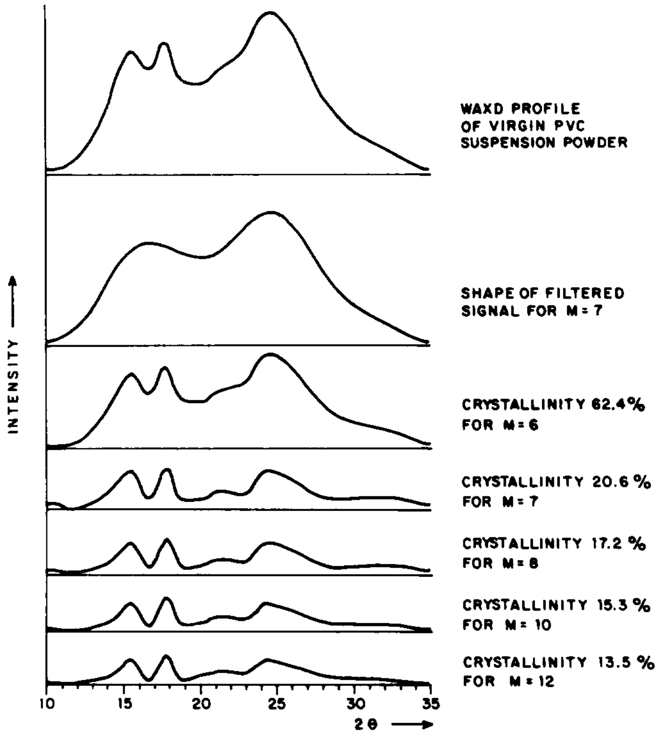

Figure 16 Fourier-transform filter method applied to the WAXD profile of a virgin PVC commercial powder

cut-off point has changed, and values of $M \geqslant 7$ are the only practical ones. The overall profile shows two new features: (1) a broad signal in the $2\theta = 21°$ range and (2) a 200 reflection much greater in area than is to be expected, giving rise to high numerical values for the crystallinity index.

The presence of the broad reflection at $2\theta = 21°$ is as yet unaccounted for. It is more prominent in the virgin powder than after treatment of any kind, so its presence appears to be related to a structure formed preferentially during polymerization.

The distortion of the intensity relationship between the 200 and 110 reflections can be explained according to two points of view. Vickers[31] has argued that the intensity of the 110 reflection diminishes due to small rotations of the molecules along their long axis. On inspection of *Figure 16*, and taking into account that the 200 reflection is theoretically one of the less strong among the reflections in the 17 to 26° (2θ) range, an alternative explanation is that, in samples with imperfect crystallinity, there is an important contribution from the mesomorphous phase to the shape of the WAXD profile in the region of the 200 crystalline reflection. In the example of *Figure 16*, the filter is not capable of distinguishing that contribution, and therefore the 200 reflection appears broader and more intense than what the unit cell would determine. No shifting of the filtered signals eliminates this distortion. The persistent alteration of the 200 peak in all but the more crystalline WAXD profiles of PVC samples is interpreted, therefore, not as an artefact derived from the use of a filter, but as evidence for the presence of a mesomorphous phase in these types of PVC samples, whose contribution to the overall WAXD profile cannot be totally filtered using the present equation. As shown in *Figure 17*, the present filter will alter a type 2 profile in such a way as to make it very similar to a type 1 profile, with respect to peak positions and peak widths. Since a type 1 profile will never give the expected intensity ratio for the 200 and 110 reflections on subtraction from a type B profile, then this would explain the distortion of the 200 reflection observed in *Figure 16*.

CONCLUSIONS

Crystallinity values of PVC samples are at best a general indication of the internal ordering of the polymer. Small crystallite sizes, the presence of a mesomorphic phase, the possible modifications to the unit cell[31] and a certain propensity to orient in the plane of the film, all contribute to the uncertainty of the measure.

Sample preparation prior to measuring the WAXD profile has been shown to influence the observed diffraction pattern. It is not only a problem of avoiding unwanted or unknown orientation effects. In the case of PVC the structure present in the virgin polymer is different from that obtained after the polymer has been solvent-cast, hot-pressed, or even after annealing with or without added plasticizer. The ratio of the intensities of the 200 and 110 reflections in WAXD patterns such as shown in *Figure 4*, and the obvious presence of a broad reflection at around $2\theta = 21°$, indicate the presence of a structure distinct from the theoretical orthorhombic unit cell in the virgin polymer. The contribution of a mesomorphous phase to such a profile is strongly suspected, and can be illustrated, as in *Figure 9*, using conventional manual curve-fitting procedures.

The type 2 amorphous profile, which served as a basis for the manual curve fit reported in *Figure 9*, is not simply a graphical convenience to obtain the necessary intensity relationship between the 200 and 110 reflections. Amorphous profiles with a narrower peak centred in the

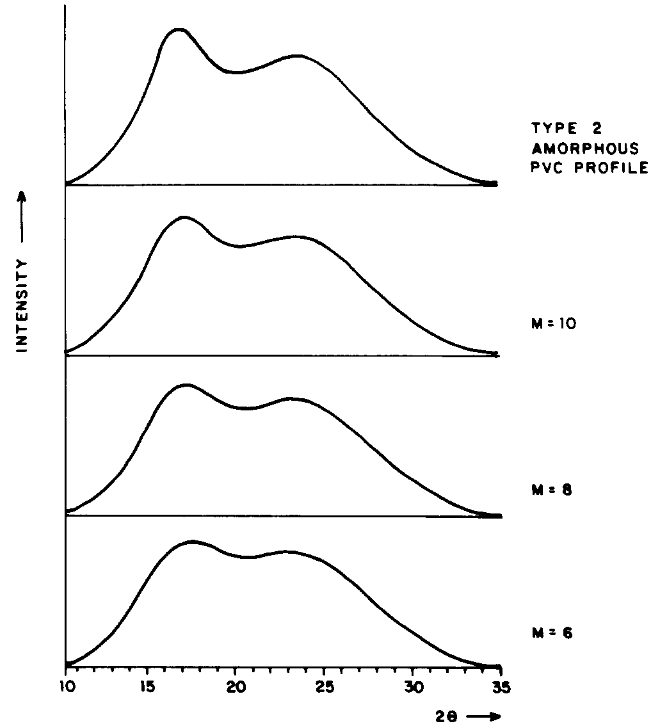

Figure 17 Evolution of a type 2 amorphous profile after filtering at different values of *M*

range $2\theta = 16$ to 17° are the WAXD profiles observed on chlorinating PVC (one such curve is reported in ref. 27). This type of profile is obtained as soon as the distinct 200 and 110 reflections disappear on increasing the chlorine content. It is analogous in peak position to the WAXD profile of PVC measured at 180°C[10], and also it correlates to the type of 'amorphous' profile generated manually in the curve-fitting procedure illustrated in *Figure 9*. All this is strong, even if as yet indirect, evidence in favour of analysing type B WAXD profiles of PVC taking into account the contribution to the overall scatter of the mesomorphous phase. In manual curve-fitting procedures, the suggested practice would be to use a non-crystalline WAXD profile with the first peak maximum at $2\theta = 17°$. The correct height and position of this peak has to be correlated with the resulting intensity ratio of the 200 and 110 reflections, which appear in the crystalline profile after subtraction. Programs can be written for personal computers to carry out this type of interactive curve fitting. The problem remains regarding the possible subjective bias still present in such a procedure.

The effort to find a more objective method that would take into account all these qualifiers gave rise to the application of a Fourier-transform filtering technique, on the assumption that the samples have no residual orientation. The method as applied does not claim the theoretical scope of other methods proposed in the literature[33] to calculate crystallinity in polymers. However, it is a pragmatic approach to the everyday problem of determining crystallinity in PVC samples. Good results have been obtained for various types of polymers, and also for the more crystalline PVC samples. The limitations of the filter function used so far in the case of the less crystalline PVC profiles reinforces the conclusion already arrived at through the more traditional approach, that in this type of curve the contribution from the mesomorphous phase present in the samples introduces a distortion in the relative intensity values of the 200 and 110 reflections which necessarily has to be accounted for in order to avoid obtaining numerical results that do not reflect the true values of the crystallinity indices of the samples.

ACKNOWLEDGEMENTS

Experimental PVC WAXD profiles used as examples in this paper correspond to previous research carried out by one of the authors (SJG) under the auspices of a CONICIT research grant at the Universidad Simón Bolívar, Venezuela. The same author would like to thank Mary Vickers of BP Research Centre, Sunbury on Thames, England, for supplying details on her past work on WAXD profiles of PVC. Finally, our thanks to Intevep SA for permission to publish the results.

REFERENCES

1 Alfrey, T., Wiederhorn, N., Stein, R. and Tobolsky, A. *Ind. Eng. Chem.* 1949, **41**, 701
2 Horsley, R. A. in 'Plastics Progress 1957', (Ed. P. Morgan), Iliffe, London, 1958
3 Natta, G. and Corradini, P. *J. Polym. Sci.* 1956, **20**, 251
4 Fordham, J. W. L., Burleigh, P. H. and Sturm, C. L. *J. Polym. Sci.* 1959, **26**, 73
5 White, D. M. *J. Am. Chem. Soc.* 1960, **82**, 5678
6 Burleigh, P. H. *J. Am. Chem. Soc.* 1960, **82**, 749
7 Rosen, I., Burleigh, P. H. and Gillespie, J. F. *J. Polym. Sci.* 1961, **54**, 31
8 Wilkes, C. E., Folt, V. L. and Krimm, S. *Macromolecules* 1973, **6**, 235
9 Lemstra, P., Keller, A. and Cudby, M. *J. Polym. Sci., Polym. Phys. Edn.* 1978, **14**, 39
10 Guerrero, S. J., Keller, A., Soni, P. L. and Geil, P. H. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 1533
11 Mammi, M. and Nardi, V. *Nature* 1963, **199**, 247
12 Lebedev, V. P., Okladnov, N. A. and Shlykova, M. N. *Vysokomol. Soed. (A)* 1967, **9**, 495
13 Baker, C., Maddams, W. F. and Preedy, J. E. *J. Polym. Sci., Polym. Phys. Edn.* 1977, **15**, 1041
14 Gilbert, M. and Vyvoda, J. C. *Polymer* 1978, **19**, 862
15 Biais, R., Geny, C., Mordini, C. and Carrega, M. *Br. Polym. J.* 1980, 179
16 Guerrero, S. J., Meader, S. and Keller, A. *J. Macromol. Sci., Phys. (B)* 1981, **20**, 185
17 Mitani, R., Ogata, J. and Awaya, H. *J. Polym. Sci., Polym. Chem. Edn.* 1973, **11**, 2653
18 D'Amato, R. J. and Strella, S. *Appl. Polym. Symp.* 1969, **8**, 275
19 Michel, A. and Guyot, A. *J. Polym. Sci. (C)* 1971, **33**, 75
20 Rayner, L. S. and Small, P. A. Br. Pat. 847676, 19??
21 Gouinlock, E. V. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 961
22 Wenig, W. *J. Polym. Sci., Polym. Phys. Edn.* 1978, **16**, 1635
23 Chartoff, R. P., Lo, T. S. K., Harrell, E. R. and Roe, R. J. *J. Macromol. Sci., Phys. (B)* 1981, **20**, 287
24 Singh, P. and Lyngaae-Jorgensen, J. *J. Macromol. Sci., Phys. (B)* 1981, **19**, 177
25 Gilbert, M. and Ansari, K. E. *J. Appl. Polym. Sci.* 1982, **27**, 2553
26 Liu, Z. and Gilbert, M. *Polymer* 1987, **28**, 1303
27 Guerrero, S. J. *J. Appl. Polym. Sci.* 1989, **38**, 923
28 Guerrero, S. J. *Macromolecules* 1989, **22**, 3420
29 Guerrero, S. J., PhD Thesis, University of Bristol, 1980
30 Brightman, E. O. 'The Fast Fourier Transform', Prentice-Hall, Englewood Cliffs, NJ, 1974
31 Vickers, M. E., private communication
32 Maddams, W. F. *Appl. Spectrosc.* 1980, **34**, 3
33 Ruland, W. *Acta Crystallogr.* 1961, **14**, 1180