Communications to the Editor

Comments on Paper "Raman Spectroscopy Employed for the Determination of the Intermediate Phase in Polyethylene"[1]

L. Mandelkern* and R. G. Alamo

Department of Chemistry and Institute of Molecular Biophysics, Florida State University, Tallahassee, Florida 32306-3015

Received December 16, 1994
Revised Manuscript Received January 10, 1995

It was claimed in a recent paper[1] that the presence of a third phase in the polyethylenes, based on Raman spectroscopy, could be seriously questioned. Since this technique has been widely used for the structural analyses of this class of polymers, it is important that this claim be seriously examined. The basis for the method was set forth originally by Strobl and Hagedorn.[2] With some modifications it has been extensively used by us[3–5] and others[6–8] to establish the phase structure of polyethylenes in the solid state. Four Raman bands were used by the investigators in ref 1 to reach their conclusion. These bands are located at 1060, 1080, 1305, and 1415 cm^{-1}. In what follows we shall discuss each of these bands in turn.

The 1080 cm^{-1} band is assigned to the liquidlike region and was used in the initial studies to quantify this region in the crystalline polymers.[2,3] However, it was found subsequently that this band was inadequate for the purpose at hand, and the reasons were explicitly stated.[4] The band at 1080 cm^{-1} varies in shape and height, depending on crystallization conditions, and is, therefore, unsuitable for use in this connection. The authors in ref 1 recognize the complexities and uncertainties that are involved in using this band. In fact, they discuss its shortcomings in more detail than was done heretofore. However, their strong statement that the Raman method is inadequate to characterize the amount of interphase is based in large measure on the previous use of this band.

The 1060 cm^{-1} band, which is assigned to the crystalline state, is used for the first time in ref 1 for the quantitative analysis of the phase structure. There is a serious question as to whether the linear relation that was used between the intensity of this band and the crystallinity level is valid. Snyder[9] has found a nonlinear relation between the intensity of bands in this spectral region and the amount of conformational disorder in the chain. Therefore, extreme caution must be exercised in interpreting this band. This point is further emphasized by examining the Raman spectra for $C_{36}H_{74}$ given in parts a and b of Figure 4 of ref 1. At 75 °C, a temperature at which $C_{36}H_{74}$ is molten, the 1415 cm^{-1} band assigned to the crystalline core has completely disappeared, as expected. However, the 1060 cm^{-1} band is clearly visible at this temperature and is still discernable at 80 °C. Since clearly this band is measuring more than the crystalline fraction, it should not be used at this time for a quantitative analysis of the crystalline portion of polyethylenes.

The theoretical uncertainties and experimental inadequacies in interpreting the 1060 and 1080 cm^{-1} bands make it prudent that they not be used at the present time for quantitative analysis of the phase structure of polyethylenes. However, the bands at 1415 and 1305 cm^{-1} are still available, their theoretical basis is sound, and they have been found to be adequate for the analysis of the polyethylene phase structure. The band at 1305 cm^{-1} gives a quantitative measures of the liquidlike region. The band at 1415 cm^{-1} results from crystal field splitting and is a measure of the orthorhombic unit cell content.[10–12] Utilizing these two well-understood bands, it is possible to carry out a complete analysis. The percent of the interfacial region is determined from the difference between 100 and the sum of the percent core crystallinity and liquidlike regions, as obtained from the 1415 and 1305 cm^{-1} bands, respectively.

It has been recognized by most practioners of this Raman method that the errors involved in subtracting two comparable quantities to obtain the interfacial content could be large. Experimental reports have indicated this and the errors have been clearly stated.[3,4,13] However, what is important is that the trends observed are systematic with chain structure and crystallization conditions.[3,13,14] Restricting ourselves to the two aforementioned bands, it is obvious that the interfacial contents of the LDPE and LLDPE (samples 9–16 of Table 2 in ref 1) are in the 10–20% range. They agree very closely with the values obtained for similar type samples by others.[6,8,13,15] The results for these branched polyethylenes are significantly higher than the values obtained for linear polyethylenes ((HDPE, samples 1–8) in ref 1). The linear polyethylene samples reported in ref 1 cover a relatively narrow interval in crystallinity levels, when the large range in values that could be attained with this polymer is considered. From previous work it would be expected that the interfacial contents would be small and similar to one another for the linear polymers studied in ref 1.[3,14] The interfacial contents of these linear polyethylenes are, as implied from the data of Table 2, of the same magnitude as the experimental error involved in the band deconvolution procedure. This was indicated previously for polyethylenes having similar crystallinity levels.[3] Systematic trends are better defined when a wider range in crystallinity levels of linear polyethylenes is used.[3,14] We thus can conclude that, based on the 1305 and 1415 cm^{-1} bands, the results reported in ref 1 are almost identical to those reported previously by others.

The interfacial contents of the branched polyethylenes, as reported in Table 2 of ref 1, give convincing evidence of the presence of a third phase determined by Raman spectroscopy. If only the results for the linear polyethylene samples studied by Naylor *et al.*[1] are considered, it is possible to argue, based on Raman spectroscopic evidence alone, that the existence of a third phase could be seriously questioned. However, the data reported for the branched polyethylenes[1,13] refute this claim, as do linear polyethylenes of lower crystallinity levels.[3,5,14]

Factor analyses of the Raman spectra of a set of seven linear polyethylenes, of varying crystallinity levels, have been reported recently.[16] In addition to the crystalline and liquidlike bands, the analysis of the spectra demonstrated the existence of a third component that can be attributed to the interfacial region. The spectrum of this component resembles that of the crystalline component. However, the peaks are somewhat broader and are shifted in position. This alternate method of analyzing the polyethylene Raman spectra also gives clear evidence of the existence of the interfacial region.

The presentation in ref 1 was ostensibly concerned only with the determination of the interfacial content by Raman spectroscopy. However, the conclusion that the existence of an interfacial region cannot be determined by this method could have the implication that this region does not exist. It is appropriate, therefore, briefly to examine this question. A large body of theoretical and experimental evidence, based on many different techniques, including Raman spectroscopy, has established the existence of a diffuse interfacial region in crystalline polymers. The extensive evidence that is available to support this conclusion has been recently presented.[17]

It has been found with polyethylenes as well as other polymers that the level of crystallinity determined by density is systematically greater than that obtained from the enthalpy of fusion.[18,19] This difference is equal to the interfacial fraction as determined by Raman spectroscopy.[18] The crystallinity levels determined from the enthalpy of fusion and those obtained from the 1415 cm^{-1} band are in good agreement. Based on the literature reports, therefore, it is not surprising that the crystallinity levels determined from the 1415 cm^{-1} band in ref 1 do not correlate with the values determined from the density, except at the high levels. This is because the 1415 cm^{-1} band only represents the core crystallinity level. This result is thus to be expected.

Carbon-13 NMR chemical shifts and relaxation times have yielded quantitative information about the interfacial region in polyethylenes.[20-22] The Raman spectra and ^{13}C NMR$-T_1$ relaxation times were determined on the same linear polyethylene samples.[21] Excellent agreement was obtained between the two methods for the interfacial content of each sample. The observed ^{13}C NMR spectrum can be unambiguously resolved into three components, each with a definite chemical shift and relaxation time.[20,22] The results are in good agreement with those expected from the analysis of the Raman internal modes. The broad-line proton NMR spectra can also be decomposed into three components.[23-26] The interfacial contents deduced by this method fit very nicely into the pattern of other results that has evolved.[17]

In summary, the results obtained for the fraction of the interphase of polyethylenes are consistent among different experimental techniques. These include previous analysis of the Raman internal modes as well as the data reported in ref 1.

References and Notes

(1) Naylor, C. C.; Meier, R. J.; Kip, B. J.; Williams, K. P. J.; Mason, S. M.; Conroy, N.; Gerrard, D. L. *Macromolecules* **1995**, *28*, 0000.

(2) Strobl, G. R.; Hagedorn, W. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1181.

(3) Glotin, M.; Mandelkern, L. *Colloid Polym. Sci.* **1982**, *260*, 182.

(4) Mandelkern, L.; Peacock, A. J. *Polym. Bull.* **1986**, *16*, 529.

(5) Failla, M.; Alamo, R. G.; Mandelkern, L. *Polym. Testing* **1992**, *11*, 151.

(6) Clas, S.-D.; Heyding, R. D.; McFaddin, D. C.; Russell, K. E.; Scammell-Bullock, M. V.; Kelusky, E. C.; St-Cyr, D. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 1271.

(7) Wang, J.; Pang, D.; Huang, B. *Polym. Bull.* **1990**, *24*, 241.

(8) Wang, L. H.; Porter, R. S.; Stidham, H. D.; Hsu, S. L. *Macromolecules* **1991**, *24*, 5535.

(9) Snyder, R. G.; Cameron, D. G.; Casal, H. L.; Compton, D. A. C.; Mantsch, H. H. *Biochim. Biophys. Acta* **1982**, *684*, 111.

(10) Boerio, F. J.; Koenig, J. L. *J. Chem. Phys.* **1970**, *52*, 3425.

(11) Luu, D. V.; Cambon, L.; Lapeyre, C. *J. Raman Spectrosc.* **1980**, *9*, 172.

(12) Luu, D. V.; Abenoza, M.; Rault, J. *J. Phys. (Fr.)* **1970**, *40*, 597.

(13) Alamo, R. G.; Viers, B. D.; Mandelkern, L. *Macromolecules* **1993**, *26*, 5740.

(14) Kennedy, M. A.; Peacock, A. J.; Mandelkern, L. *Macromolecules* **1994**, *27*, 5297.

(15) Benavente, R.; Pereña, J. M.; Bello, A.; Perez, E. *Br. Polym. J.* **1990**, *23*, 95.

(16) Shen, C.; Peacock, A.; Alamo, R.; Vickers, T.; Mandelkern, L.; Mann, C. *Appl. Spectrosc.* **1992**, *46*, 1226.

(17) Mandelkern, L. *Chemtracts: Macromol. Chem.* **1992**, *3*, 347.

(18) Mandelkern, L. *Polym. J.* **1985**, *17*, 337.

(19) Mandelkern, L. *Acc. Chem. Res.* **1990**, *23*, 380.

(20) Saito, S.; Moteki, Y.; Nakagawa, M.; Horii, F.; Kitamaru, R. *Macromolecules* **1990**, *23*, 3256.

(21) Axelson, D. E.; Russell, K. E. *Prog. Polym. Sci.* **1985**, *11*, 221.

(22) Cheng, J.; Fone, M.; Reddy, V. N.; Schwartz, K. B.; Fischer, H. P.; Wunderlich, B. *J. Polym. Sci., Part B: Polym. Phys.* **1994**, *32*, 2683.

(23) Bergmann, K.; Nawotki, K. *Kolloid Z-Z. Polym.* **1967**, *219*, 132.

(24) Bergmann, K.; Nawotki, K. *Kolloid Z-Z. Polym.* **1973**, *251*, 962.

(25) Kitamaru, R.; Horii, F.; Hyon, S.-H. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 821.

(26) Kitamaru, R.; Horii, F. *Adv. Polym. Sci.* **1978**, *26*, 139.

MA945063E