# Response to the Comment on "Raman Spectroscopy Employed for the Determination of the Intermediate Phase in Polyethylene" by Naylor et al.

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In this reply we respond to the comments made by Mandelkern and Alamo[1] to our paper with the above title, viz., ref 2. By some unfortunate circumstances, not due to the authors, we were unable to reply to Prof. Mandelkern's and Dr. Alamo's comments before. Here we would like to take the opportunity to present our reply.

In the abstract of ref 2 we formulated our main conclusions, i.e. "The present results indicate that the quantification of a third, interlamellar, phase in polyethylene is not possible when based on standard Raman spectra". Regarding the latter, we referred to the Strobl and Hagedorn method.[3] Our conclusion evidently contrasts to those put forward by other authors who have committed themselves to rather firm statements concerning the existence *and* quantifiability of an interlamellar phase in semicrystalline polyethylene based on Raman spectroscopy.[4]

Referring to our experience, working at two independent industrial research laboratories, during the first phase of a joint BP–DSM project our attention was unequivocally drawn to inconsistencies in prior interpretations of Raman results. While initially working independently, using different types of spectrometers, i.e., a grating instrument and an FT-Raman instrument, it became very clear that the results concerning quantification of an interlamellar phase are not at all unambiguous. Two facts played a decisive role: first, the collaboration between two basically independent groups, which were each aiming at the straightforward application of the Strobl and Hagedorn method, and, more importantly, the use, for the first time reported, of an FT-Raman instrument which requires much less data correction. Our results have clearly shown that major differences in, e.g., crystallinity can be found when applying the same method of analysis to data from the grating instrument and the FT-Raman instrument, respectively (see Table 2 of ref 2), while accounting for the sensitivity of the various parts in the grating instrument in the best possible way. Regarding the data analysis and the type of original spectra employed, we claim to have reported an unprecedented state-of-the-art data analysis.

We argue that the Strobl and Hagedorn method suffers from the assumption that the Raman spectrum of the amorphous phase is taken equal to that of the liquid phase. This is by no means trivial, and in fact it is incorrect. Moreover, there is interference of remaining intensity at the "crystalline" 1060 and 1130 $\text{cm}^{-1}$ positions in the spectrum of the liquid phase. These items have not been addressed by Mandelkern and Alamo or by others. Temperature dependences of the liquid phase spectrum were addressed in ref 2 and need to be taken into account when using the liquid phase spectrum as the reference of what should be the amorphous phase spectrum.

Mandelkern and Alamo are correct when they state that the inadequacy of using the 1080 $\text{cm}^{-1}$ band has been pointed out before but also note that its shortcomings were discussed by us in more detail than was done heretofore. We also seem to agree on the inappropriateness of using the 1060 $\text{cm}^{-1}$ band for the purpose of quantifying an interlamellar phase. Even though the statements presented by Mandelkern and Alamo regarding the 1415 and the 1305 $\text{cm}^{-1}$ bands are sound and the fundamental interpretations might be agreed upon, the major practical difficulty arising while analyzing the Raman spectra is to unravel, unambiguously and in a pertinent *quantitative* way, this region of highly overlapping bands. It is at this point that we definitely seem to disagree with Mandelkern and Alamo.

Mandelkern and Alamo have also argued that "Systematic trends are better defined when a wider range in crystallinity levels of linear polyethylenes is used".[1] For the linear polyethylenes employed in our study, the crystallinity varied from 33 up to 56% taking mass crystallinity and from 13 up to 47% taking the crystallinity derived on the basis of the 1415 $\text{cm}^{-1}$ Raman band and the analysis using Voigt band profiles applied to the data obtained using the grating instrument. The 1415 $\text{cm}^{-1}$ band is a band favored by Mandelkern and Alamo for demonstrating the existence of the interlamellar phase in polyethylene. Considering *all* samples from our study, the crystallinity varies from 33 up to 75% according to mass crystallinity and from 13 up to 72% using the 1415 $\text{cm}^{-1}$ Raman band. Despite the fact that we employed 16 different samples with a widely varying crystallinity, honesty prevents us from arriving at the conclusion that we would have found clear-cut evidence for the existence and quantification of an interlamellar phase.

What we must interpret as a serious allegation is presented by Mandelkern and Alamo when they use the phrasing "The presentation in ref 1 [note: this is our paper, currently ref 2] 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". We most definitely object to Mandelkern et al. using the word *ostensibly*. We emphasize that there is, according to our view, no discussion about the existence of an *interface*. The real question is whether, and this is what Mandelkern et al. have also addressed, there is *an identifiable and quantifiable* interlamellar *phase* in semicrystalline polymers, e.g., polyethylene. Our current results, viz., ref 2, infer that the Strobl and Hagedorn method does not yield a positive answer.

## References and Notes

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(4) Mandelkern, L. *CHEMTRACTS—Macromol. Chem.* **1992**, *3*, 347.

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