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Comment on "Observation of mutual diffusion of macromolecules in PS/PMMA binary films by confocal Raman microscopy" by C. Hu, X. Chen, J. Chen, W. Zhang and M. Q. Zhang, *Soft Matter*, 2012, 8, 4780

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A paper by Hu *et al.* (*Soft Matter*, 2012, 8, 4780) reports on the use of confocal Raman microscopy to resolve mutual diffusion between polystyrene (PS) and poly(methyl methacrylate) (PMMA). In-depth optical sectioning is employed to measure the diffusive broadening of the originally planar PS–PMMA interface, from which tracer and mutual diffusion coefficients and values for the PS–PMMA thermodynamic interaction parameter are extracted. Here, a reinterpretation of Hu's data that leads to a completely different scenario is presented, as apparent diffusive broadening can be mostly attributed to optical distortions inherent to the probe methodology. It also explains the lack of consistency of kinetic and thermodynamic parameters obtained by the authors from their diffusion analysis in comparison with earlier published data on this system. Overall, it highlights the importance of carrying out appropriate data analysis when confocal Raman microscopy is applied in dry depth-profiling investigations.

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In a recent paper, Hu and co-workers reported experiments of interdiffusion between polystyrene (PS) and poly(methyl methacrylate) (PMMA) using confocal Raman microscopy as a primary experimental tool.¹ Raman intensity profiles for each of the components were measured by in-depth optical sectioning of the interfacial region and subsequently converted to binary diffusion profiles. Kinetic parameters (mutual and tracer diffusion coefficients) and thermodynamic data (Flory–Huggins interaction parameter χ) for the PS–PMMA polymer pair were obtained from analysis carried out in the context of Fickian diffusion models, including some of them developed in the past to describe mutual diffusion in miscible polymer pairs.

My comments are concerned with the interpretation of Raman microscopy data carried out by the authors as well as with their analysis of polymer diffusion performed. Hu *et al.* used the technique to resolve diffusive transport of PS and PMMA chains at the contact interface. PS and PMMA samples employed had relatively high molecular weights, $M_w = 171\,000$ and $57\,000\text{ g mol}^{-1}$ respectively, above that critical to form entanglements, and glass transition temperatures (T_g) of $98\text{ }^\circ\text{C}$ and $124\text{ }^\circ\text{C}$. Hu's approach consisted in the preparation of PS and PMMA polymer slabs of about $15\text{ }\mu\text{m}$ thick, subsequently

placed in contact to produce a planar interface. Specimens were annealed for 48 hours in the temperature range between 130 and $150\text{ }^\circ\text{C}$. Polymer diffusion was followed by probing the PS–PMMA contact region *via* confocal Raman depth profiling through the transparent PS layer using a conventional metallurgical objective (dry optics configuration).

Overall, it has been well documented that dry optics induces optical aberrations, mostly arising from laser refraction at the sample surface, that distort depth profiling measurements in several ways.^{2,3} Specifically, (i) the depth scale is artificially compressed, by a factor between 1.5 and 2, depending on the refractive index (n) of the sample; (ii) depth resolution worsens as one focuses deeper into the sample, well beyond the theoretical limit predicted by diffraction theory. The quantitative modelling of these effects in the context of Raman depth profiling has been addressed by several authors.^{2–4} Experimental approaches to characterize depth responses have also been published.^{5,6} Appendix I presents calculations of depth responses (point spread functions, PSF) for different focusing depths, in conditions comparable to those of Hu' experiments. Simulations indicate that the depth scale is compressed by a factor of 1.7 and that depth resolution worsens from $4\text{ }\mu\text{m}$ at the sample surface to about $9\text{ }\mu\text{m}$ when focusing $15\text{ }\mu\text{m}$ below. These results are in excellent agreement with those obtained experimentally.^{5–7} Appendix I also illustrates how these optical distortions affect step profiles in the conditions of Hu' measurements.

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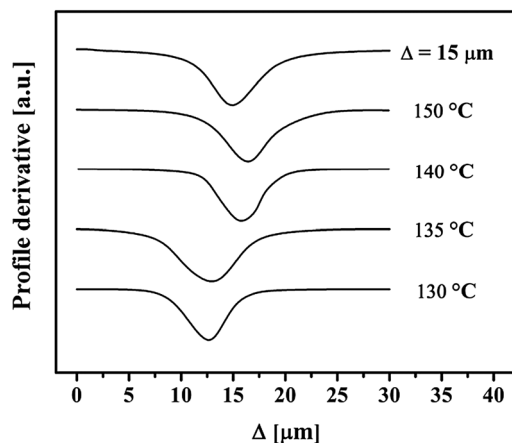


Fig. 1 Raman intensity profile derivatives, as taken from Fig. 5(a) of Hu's paper. The top curve represents PSF for the present acquisition conditions.

Although the authors have been aware of these technical issues, commented in the "CRM measurements" section of their paper, they have not taken precautions to properly deal with them: (i) rescaling factors for the depth scale have been omitted which implies that all the profiles reported are artificially compressed by a factor of about 1.7; (ii) depth resolution has not been correctly characterized in any of the experiments, so it is hard to resolve genuine mass transport from artificial interfacial broadening. Details on these and other conflictive issues of Hu' data are given in Appendix II.

The analysis of Raman intensity profiles of the diffused samples reported in Fig. 5 by Hu *et al.* allows appreciation of how the lack of enough depth resolution to resolve mass transport impacts data interpretation. For instance, we observe that the diffusive broadening is surprisingly similar for all the annealing temperatures, and below 10 μm (uncorrected depth scale) in all the cases. Fig. 1 makes clear this issue by comparing the profile derivatives of the data reported in Fig. 5(a) of Hu's paper, represented in the domain of the uncorrected (or apparent) depth scale (Δ). It can be seen that the apparent interfacial width is indeed similar for all the samples, confirming that broadening is not thermally activated. The top curve in Fig. 1 corresponds to the predicted PSF for a nominal focusing depth of about 15 μm ; for an appropriate comparison, the depth scale of PSF has been compressed by a factor of 1.7. That PSF can be taken as a representation of the minimum diffusive broadening detectable in the present instrumental conditions. Clearly, the width of the responses is also comparable with that of PSF. It would indicate that the sigmoidal shape of the intensity profiles (Fig. 5) that Hu ascribes to diffusion by resemblance with predictions of the Fick's law is actually due to optical distortions of the most likely sharp interface (see also Fig. 3 in Appendix I). Overall, Raman data do not support substantial diffusive transport, but, on the contrary, lack of it, at least in the scale of spatial discrimination of the technique.

All the above observations may well explain the unrealistic values for the kinetic and thermodynamic parameters for the PS-PMMA pair obtained by the authors from their analysis of

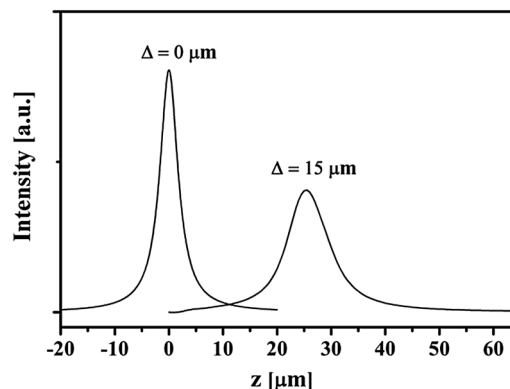


Fig. 2 Calculated PSF for two different nominal focusing depths, in the operative conditions of Hu's paper.

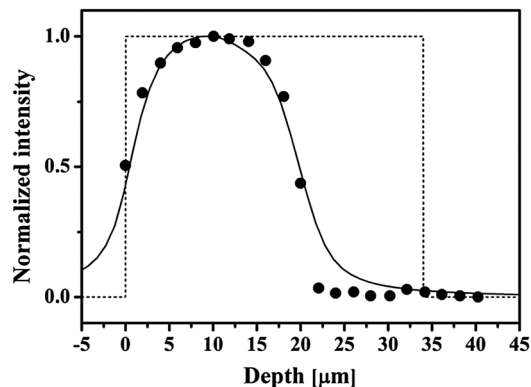


Fig. 3 Calculated Raman depth-response of a film 34 μm thick (solid line), compared with the true response (dotted line). Symbols correspond to data taken from Fig. 3(b) of Hu's paper. The zero in the depth scale corresponds to the outer air/film interface whereas positive values indicate focusing within the film.

polymer diffusion (see Appendix III). One particularly critical example are the negative values of χ reported for the PS-PMMA pair, which would imply that the polymer pair is fully miscible, contradicting the authors' own statement, which introduces this polymer pair as *immiscible*. Actually, PS-PMMA is characterized by an upper critical solution temperature phase diagram and by a positive temperature-dependent χ parameter.⁸⁻¹⁰ For the molecular weights and temperatures studied by Hu, thermodynamics predicts that the system is immiscible,[†] so eventual diffusion proceeds in the coexistence region. This particular diffusion case has been studied by several authors.¹¹⁻¹⁴ Mass transport was observed to evolve till the coexisting equilibrium compositions are reached, *via* a complex, non-Fickian dynamics.^{11,12} Experiments carried

[†] The minimum value of χ that produces phase separation is given by Flory-Huggins theory as $\chi_{\text{spc}} = 0.5 (N_{\text{PS}}^{-0.5} + N_{\text{PMMA}}^{-0.5})^2$. If $\chi > \chi_{\text{spc}}$ the equilibrium state is that of two coexisting phases, whereas $\chi < \chi_{\text{spc}}$ indicates full miscibility. For PS-PMMA, χ values measured by Paul *et al.* as $\chi = (0.021 + 3.2/T)$ have been taken as representative.¹⁰ In the conditions of Hu's work, $\chi_{\text{spc}} = 0.0022$, whereas for the range of annealing temperatures 130-150 $^{\circ}\text{C}$ χ is predicted to be about 0.029. As $\chi_{\text{spc}} < \chi$, the system studied by Hu is very likely in the region of phase separation.

out by Fernandez *et al.* and Kressler *et al.* have shown that the PS–PMMA interface in the coexistence region, for samples, times and annealing temperatures equivalent to those of Hu, is in the range 2–5 nm.^{13,14} These values are in agreement with those predicted by the Helfand–Tagami theory, below 3 nm for PS–PMMA.¹⁵ That level of polymer interdiffusion is certainly far below the resolution power of confocal Raman microscopy, that delivers, in optimum diffraction-limited conditions, spatial resolutions above 200 nm.¹⁶

In summary, although confocal Raman microscopy is a valuable technique, its level of spatial resolution is not enough to resolve polymer diffusion in immiscible polymer pairs. The purported diffusion profiles measured by the authors can be ascribed to optical distortions, which highlights the importance of carrying out appropriate data analysis when confocal Raman microscopy is applied in dry depth-profiling investigations. It also explains the lack of consistency of kinetic and thermodynamic parameters obtained by the authors from their diffusion analysis in comparison with earlier published data on this system.

Appendix I

Fig. 2 shows the predicted depth response or point spread function (PSF) in the conditions employed by Hu *et al.*; that is, a sample of $n = 1.5$ is examined with a 514 nm laser through a 0.75 NA (numerical aperture) dry objective. The calculation scheme for PSF accounts for on-axis diffraction, refraction and effect of pinhole aperture (see details elsewhere).³ PSF are represented in the real depth scale (z), for two nominal (or apparent) values of focusing depth (Δ), as measured from the scale of the microscope stage. In any of the scales, zero corresponds to the sample surface whereas positive values indicate focusing depths below the sample surface (or within the sample). At the sample surface ($\Delta = 0 \mu\text{m}$), depth resolution, as measured from the full width at the half maximum (FWHM) of PSF, is about 4 μm . When focusing 15 μm below the sample surface, the laser beam deviates at the air/sample interface due to refraction and spreads over a rather large region (15–35 μm) that increases the PSF width. The real focus point is shifted much deeper than the place where the laser beam was originally directed (15 μm) giving rise to the above-mentioned apparent compression of the depth scale. A direct comparison with experimental PSF data can be found elsewhere.⁵

Fig. 3 illustrates how a 34 μm thick film would look when it is depth profiled in the conditions of Hu's experiment. The true response is represented by a dotted line by a step function 34 μm in width. Its convolution with the predicted PSF generates the apparent or *as-measured* response (solid line); the details of the calculations can be found elsewhere.³ It is observed that the film looks artificially thinned, with an apparent thickness of about 20 μm ; that is, it appears compressed by a factor of about 1.7. Sharp sample features, such air–polymer interfaces, appear rounded and extended over a region of about 10 μm for the case of the deep interface, reflecting limitations of the technique in resolving even micron-sized sample features. The calculations of

apparent responses *via* convolution are very realistic and agree very well with experimental observations, as shown in an earlier work.^{3,7} For instance, the predicted response shows very good matching with the data of Fig. 3(b) of Hu's paper (solid circles), corresponding to the Raman depth profile of a single PS film with an apparent thickness of 20 μm .

Appendix II

(i) The lack of using rescaling factors for the depth scale not only affects the diffusion coordinate, essential for a well-based quantitative analysis, but it also creates conflict when comparing Raman data with cross section film images reported by Hu *et al.*: while Raman data indicate an apparent thickness of 20 μm (Fig. 3 of Hu's paper), the real film thickness should be above 30 μm , a value 2 times larger than those seen in their SEM images of Fig. 4.

(ii) The authors attempted to experimentally quantify the operative depth resolution in the sample by tracing the laser spot image at different focusing depths, as shown in Fig. 3(c) of their paper. However, they have based their analysis on images of the lateral (x, y) dimension of the laser spot, instead of that relevant to the characterization of depth resolution (z).

(iii) The expression used by Hu *et al.* to convert spectral information to local weight fractions (eqn (4) of their paper), adapted from an earlier work of infrared spectroscopy, is not applicable to Raman spectroscopy. In Raman spectroscopy, the relationship between mass concentration and peak intensity is linear, not logarithmic, as seems to be implied by eqn (4).

(iv) In the diffusion profiles reported in Fig. 6 of Hu's paper the sum of weight fractions of PS and PMMA components does not equal one as it should be in the case of binary diffusion, which is most likely due to the incorrect logarithmic term used to translate Raman intensity to concentration.

Appendix III

(i) Hu *et al.* report in Table 1 values for tracer diffusion coefficients (D^*) for PS in pure PMMA between 1.27×10^{-14} and $1.7 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$. Similarly, D^* for PMMA chains in pure PS were found to be in the range 1.97×10^{-13} – $3.12 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$. These data can be compared with those obtained by Shearmur *et al.* on the same polymer pair, but with samples having much lower molecular weights: 4550 g mol^{-1} for PS and 3100 g mol^{-1} for PMMA.¹⁷ The values of D^* reported by Shearmur are in the range between 10^{-16} and $10^{-18} \text{ cm}^2 \text{ s}^{-1}$ for PS, and 10^{-13} and $10^{-14} \text{ cm}^2 \text{ s}^{-1}$ for PMMA, in comparable ranges of $T-T_g$ values. The correction for differences in molecular weight between experiments, carried out by reptation theory, yields values of D^* in the range 10^{-20} – $10^{-21} \text{ cm}^2 \text{ s}^{-1}$ for PS and 10^{-14} – $10^{-16} \text{ cm}^2 \text{ s}^{-1}$ for PMMA, which are orders of magnitude smaller than those reported by Hu.

(ii) The response of D^* with temperature shown in Fig. 7 of Hu's paper does not agree with that reported by Shearmur. While data of Shearmur reflect changes in D^* by factors of

20 for PS and 55 for PMMA, Hu's reports show small variations, 1.3 for PS and 1.6 for PMMA, in similar $T-T_g$ ranges.

(iii) Hu *et al.* obtained values of the Flory–Huggins χ parameter from the comparison of experimental data with theoretical expressions for mutual diffusion coefficients. Values reported by Hu *et al.* in Table 3 for the PS–PMMA polymer pair are negative, in contrast to the positive values reported in several earlier studies.^{8–10}

(iv) For the range of annealing temperatures 130–150 °C used by Hu *et al.*, $\chi > \chi_{\text{spc}}$, so their system is very likely in the region of phase separation.[†] It puts in question the models used by Hu to analyze mutual diffusion, based on a simple form for the free energy term, more suitable for conditions of full miscibility.¹⁸ A sign of this inconsistency can be seen in eqn (9) of Hu's paper: on the basis of a correct value for the χ parameter, as $\chi > \chi_{\text{spc}}$, eqn (9) predicts negative values for the interdiffusion coefficients, a clear indication that this type of diffusion models are not appropriate for this case.

Acknowledgements

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