

Soft Matter

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Reply to the ‘Comment on "Observation of mutual diffusion of macromolecules in PS/PMMA binary films by confocal Raman microscopy"’ by J. Pablo Tomba, *Soft Matter*, 2016, 12, DOI: 10.1039/C5SM02735G

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Abstract

We greatly appreciate Tomba’s valuable comments on our paper appearing in *Soft Matter* (2012, vol.8, p.4780). Our responses are listed below to provide additional information for academic discussion.

We agree with Tomba’s point of view that optical distortion would present in the experiments, but the investigation of mutual diffusion of macromolecules in binary films using confocal Raman microscopy (CRM) depth profiling with dry objective should still be a feasible method. The conclusion is supported by the following results of other groups using different techniques.

(i) Yarwood and co-workers conducted molecular depth profiling study of PMMA/PVOH laminated on quartz using CRM with dry objective.^{1,2} Hydrogen-bonding interaction between ester and alcohol groups in the interfacial region was revealed.

(ii) Shearmur et al. studied interdiffusion of PS and PMMA by nuclear reaction analysis (NRA).³ The materials are the same as ours. They found that total miscibility between PS and PMMA is enabled under certain circumstances, which agrees with our observation. Moreover, the mutual diffusion coefficient was determined to be $6 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ for their system, which

is very close to our estimation: $5.34 \times 10^{-13} \sim 6.77 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ (of “fast theory”).

(iii) In the work by Composto et al.,⁴ diffusion coefficient of PS in miscible PS/poly(xylenyl ether) blends was measured by forward recoil spectrometry as a function of polymerization degree (N), which equals to about $5 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ when the value of our PS (N = 1710) is interpolated. Comparatively, the diffusion coefficient of PS measured by CRM was in the range $1.27 \times 10^{-14} \sim 1.70 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$. Evidently, the results resemble each other.

Moreover, Stamm et al. measured diffusion coefficient of PMMA by X-ray as a function of molecular weight.⁵ When the molecular weight of our PMMA (i.e. 57000) is interpolated, the diffusion coefficient is estimated to be about $1 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$. The value is slightly lower than those measured by CRM ($1.97 \times 10^{-13} \sim 3.12 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$), but it is understandable because the polydispersity (M_w/M_n) of our PMMA (1.56) is obviously greater than that of the PMMA used in the work of Stamm et al. (1.04~1.07). The widely polydispersed macromolecules must have affected the measurement of confocal Raman microcopy depth profiling. Supposing that the molecular weights of 10000 and 150000 (that still fall in the range of molecular distribution of our PMMA) are used for the interpolation, the diffusion coefficients are found to be about $1.5 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ and $1.0 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$, respectively. The data not only somewhat overlap the results of CRM (i.e. $1.97 \times 10^{-13} \sim 3.12 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$), but also fall in the range of diffusion coefficients measured by Shearmur et al.³ ($6.00 \times 10^{-13} \sim 1.86 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$). This comparative analysis demonstrates that the widely polydispersed molecular weight of our PMMA would result in wider range of diffusion coefficient, but it is still comparable to the results reported by other groups.

(iv) The diffusion coefficients of PS and PMMA corrected by Tomba are $10^{-20} \sim 10^{-21} \text{ cm}^2 \text{ s}^{-1}$ and $10^{-14} \sim 10^{-16} \text{ cm}^2 \text{ s}^{-1}$, respectively. Although they are smaller than those reported by us, they obey the same law as our results ($1.27 \times 10^{-14} \sim 1.7 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ for PS, $1.97 \times 10^{-13} \sim 3.12 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ for PMMA). That is, the diffusion coefficient of PS is lower than that of PMMA.

We have been aware of CRM dry depth-profiling technical issues before we carried out the experiments. Immersion objective can reduce experimental error, but we considered other two problems. (i) It is hard to find suitable oil that does not penetrate into the polymer films. So long as the oil molecules were diffused inside polymer, swelling induced size change

would greatly affect the measurement. (ii) The confocal nature of the Raman microscope significantly rejects signal from the immersion. In this context, CRM dry depth-profiling technique was selected. By taking advantage of the following factors (that have been described in our article, i.e. Soft Matter, 2012, vol.8, p.4780), nevertheless, the optical distortion was controlled at a low level.

(i) The refractive indexes of PS and PMMA are 1.550 and 1.490, respectively. The minute difference in refractive index would not induce significant change in optical path when laser enters PMMA from PS. As a result, the optical distortion originating from refraction is minimized.

(ii) The light transmittances of PS and PMMA are similar (with difference of 5 %), so that the optical distortion due to absorption should also be very low.

(iii) Considering that imperfect contact between PS and PMMA films would disfavor the interdiffusion of macromolecules and lead to Raman signal distortion at the interface, a Universal Film Maker (0016-010E, Thermo, USA) was used to prepare the specimens. Consequently, the surfaces of both PS and PMMA films are quite smooth, and no defects are observed at the interface of the binary film using scanning electronic microscope. It means that the possible interstitial gaps between PS and PMMA films are successfully removed during the fabrication, which must help to reduce optical distortion.

It is worth noting that De Luca et al. applied Raman microscopy with dry objective to the study of diffusion in polymer blend by a droplet-based system.^{6,7} They reported that dry objectives and spherical aberrations produced an indetermination on their measurements within the experimental errors.

Since depth resolution is the main factor that controls measurement error of CRM,^{8,9} the intensity response of silicon spectrum to depth profiling was measured with dry objective in the presence of refraction (514 nm laser beam was focused by a 0.75 NA, 50× metallurgical objectives. The sample was mounted on a motorized XY stage, with vertical (Z) displacement controlled by an auto micrometer adjustment on the microscope). It was found that the full width at half-height (FWHH) of silicon wafer is 3.5 μm , which represents the depth resolution. Tomba suggested in his comment that the FWHM of our sample is about 4 μm when measured by dry objective. In this context, the experimental error resulting from depth

profiling is $(4.0-3.5)/3.5 = 14.3\%$.

Besides, the accuracy of thickness measurement is $\pm 0.5\ \mu\text{m}$, meaning that the experimental error of our sample thickness measurement is $0.5/15 = 3.3\%$.

On the basis of the above estimation, it is known that the error of our CRM measurement should be less than 20 %.

References

- 1 S. Hajatdoost, J. Yarwood, *Applied Spectroscopy*, 1996, **50**, 558.
- 2 S. Hajatdoost, M. Olsthoorn, J. Yarwood, *Applied Spectroscopy*, 1997, **51**, 1784.
- 3 T. E. Shearmur, A. S. Clough, D. W. Drew, M. G. D. Van Der Grinten, R. A. Jones. *Macromolecules*, 1996, **29**, 7269.
- 4 R. J. Composto, E. J. Kramer, D. M. White. *Macromolecules*, 1998, **21**, 2580.
- 5 Y. Liu, G. Reiter, K. Kunz, M. Stamm, *Macromolecule*, 1993, **26**, 2134.
- 6 A. C. De Luca, G. Rusciano, G. Pesce, S. Caserta, S. Guido, A. Sasso, *Macromolecules*, 2008, **41**, 5512.
- 7 A. Jonáš, A. C. De Luca, G. Pesce, G. Rusciano, A. Sasso, S. Caserta, S. Guido, G. Marrucci, *Langmuir*, 2010, **26**, 14223.
- 8 N. J. Everall, *Appl. Spectrosc.* 2000, **54**, 773.
- 9 N. J. Everall, *Appl. Spectrosc.* 2000, **54**, 1515.