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Correction: Avoiding compositional drift during the RAFT copolymerization of *N*-(2-hydroxypropyl)-methacrylamide and *N*-acryloxysuccinimide: towards uniform platforms for post-polymerization modification

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Correction for 'Avoiding compositional drift during the RAFT copolymerization of *N*-(2-hydroxypropyl) methacrylamide and *N*-acryloxysuccinimide: towards uniform platforms for post-polymerization modification' by John Moraes *et al.*, *Polym. Chem.*, 2015, **6**, 3245–3251.

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The original manuscript (John Moraes *et al.*, *Polym. Chem.*, 2015, **6**, 3245–3251) discussed the reactivity ratios and copolymerization kinetics of the *N*-(2-hydroxypropyl)methacrylamide (HPMA) and *N*-acryloxysuccinimide (NAS) comonomer pair and the post-polymerization modification of a poly(HPMA-*stat*-NAS) copolymer. The aim of this correction is to point out and correct a mistake that was made in the peak assignments in Fig. S1A of the original manuscript. While this mis-assignment does not affect the analysis of the copolymerization behavior of the HPMA–NAS comonomer pair and the determination of the reactivity ratios for these two monomers, which are the key points of the paper, it does not accurately describe the post-polymerization modification of the poly(HPMA-*stat*-NAS) copolymer, which is described at the end of the manuscript.

In Fig. S1A in the ESI for our original manuscript, the peak at 3.5 ppm in the ¹H NMR spectrum of poly(HPMA-*stat*-NAS) was assigned to the CH₂ groups of NAS. This signal, however, should be assigned to H₂O. The CH₂ groups of NAS appear at 2.94 ppm. This region (2.87–3.03 ppm) is also where the solvent DMF protons appear (Fig. 1, this document). However, the solvent contribution to the peak can be subtracted using the protons at 2.72–2.86 ppm (also CH₃ from DMF). Doing this calculation yields an integral value of 1.30 for the CH₂ protons of the NAS group (*cf.* 2.16 as in the original manuscript Fig. S1A). This leads to a NAS composition of the final polymer of 25% (as opposed to 35%, which was stated in the original manuscript). The lower value suggests that some hydrolysis of the active esters may be taking place as previously noted by Religio *et al.*,¹ however it is worth noting that the authors in this case obtained the ¹H NMR spectrum in D₂O, which is expected to have a much larger potential for hydrolysis.

In the original manuscript, we reported the post-polymerization modification of a poly(HPMA-*stat*-NAS) copolymer with 2-aminomethyl-18-crown-6. This point remains as evidenced by the presence of the crown ether peaks in the ¹H NMR spectrum (3.36–3.74 ppm, original manuscript Fig. S1B). Once again however, it is worth considering the H₂O contribution to these peaks. As seen in Fig. 2A (this document), the residual water peak coincides with the crown ether peaks of 2-aminomethyl-18-crown-6 resulting in a higher than expected integral (compared to the ¹H NMR spectrum of the same compound in chloroform (Fig. 2B, this document)). In chloroform, where there is no overlap of a water peak with the crown ether resonances, the ¹H NMR signals between 3.6 and 3.9 ppm represent approximately 94% of the total crown ether integrals.

Knowing that the ¹H NMR resonances between 3.6 and 3.9 ppm account for 94% of the crown ether signal, the spectrum in Fig. S1B of the original manuscript can be re-examined. If the region from 3.60 to 3.74 ppm is integrated and considered as 94% of the crown ether integral (Fig. 3), it is found that the crown ether group is incorporated into 21% of the total number of repeat units. As the starting polymer contains 25% NAS units, this means that there is an apparent 4% loss of functionality on conversion of the active ester moieties into crown ether moieties. While these re-calculations do not affect the salient points in the paper, especially with regard to compositional drift and reactivity ratios, it is important that they are corrected so that a more accurate depiction of the polymerization and post-polymerization modification is portrayed.

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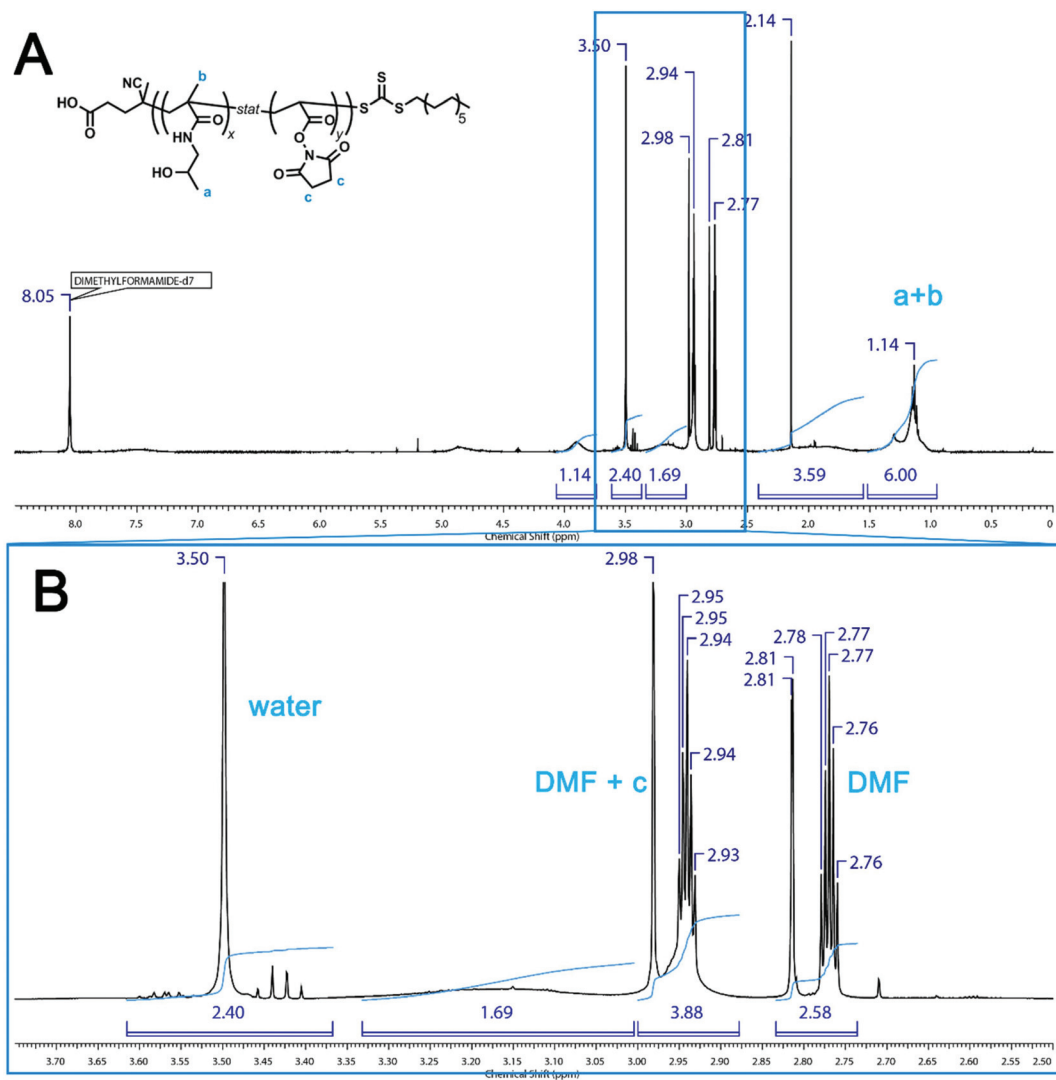


Fig. 1 ¹H NMR spectra of poly(HPMA-*stat*-NAS): (A) full spectrum and (B) zoomed in region.



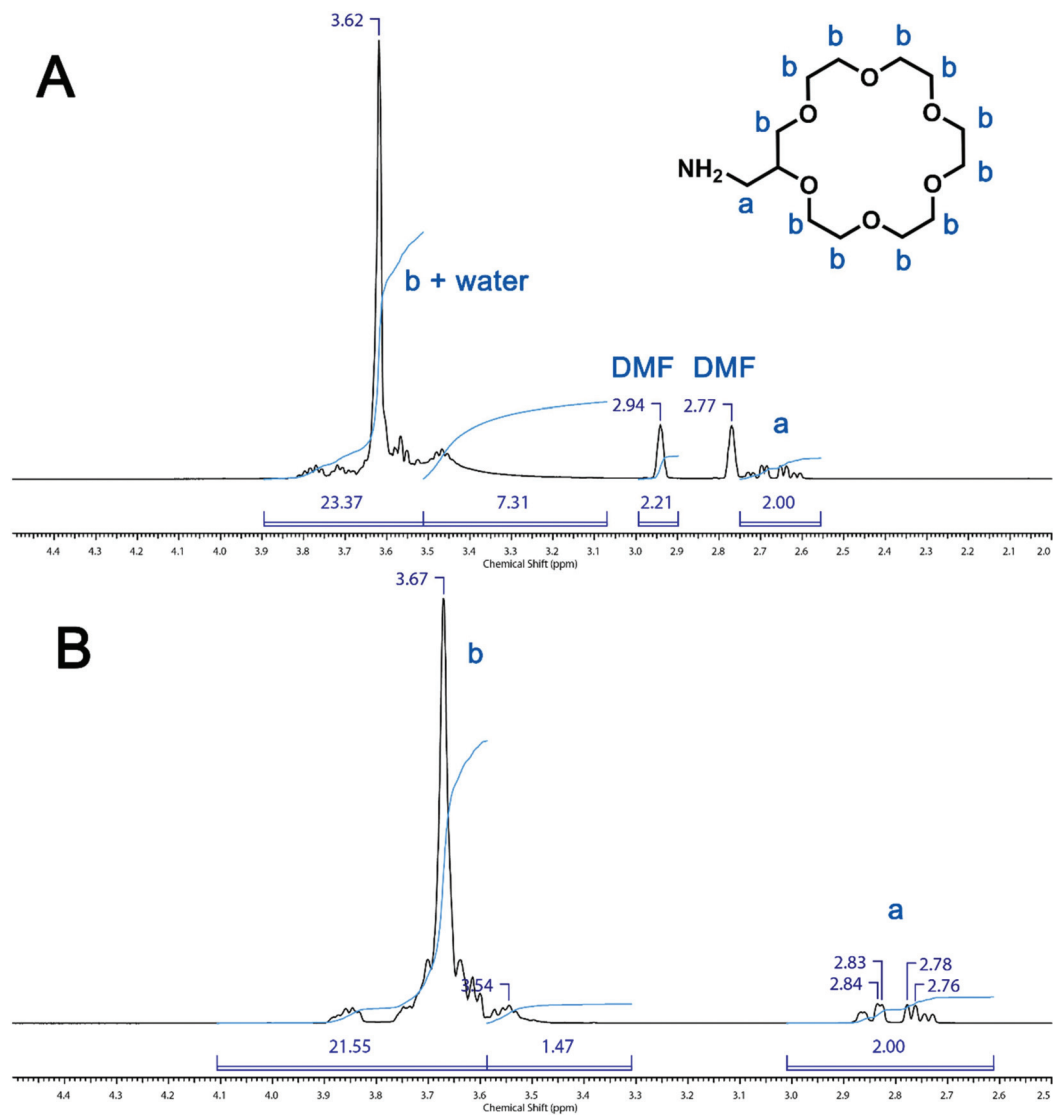


Fig. 2 ^1H NMR spectra of 2-aminomethyl-18-crown-6 in (A) DMF-d_7 and (B) CDCl_3 .



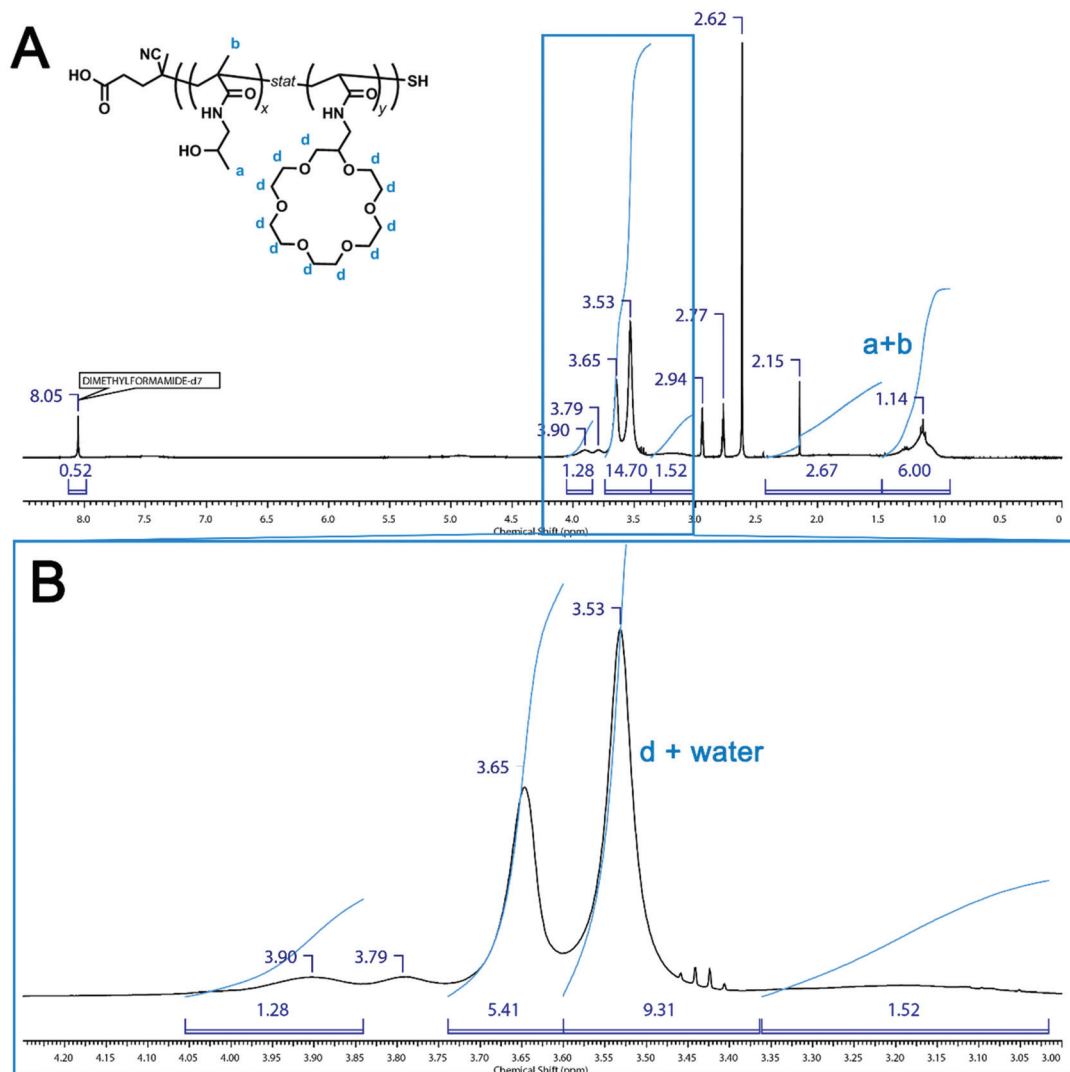


Fig. 3 ^1H NMR spectrum of poly(HPMA-*stat*-NAS) after post-polymerization modification with 2-aminomethyl-18-crown-6: (A) full spectrum and (B) zoomed in region.

In summary, a re-examination of the ^1H NMR spectra in Fig. S1 in the ESI of our original manuscript points to the distinct possibility of some hydrolysis of the active ester groups of the NAS in the poly(HPMA-*stat*-NAS) copolymer. The extent of hydrolysis is difficult to quantify, especially given the complexity of the region in the ^1H NMR spectra. However, the point in the original manuscript that near quantitative conversion of the NAS groups by the amino crown ether remains, even under this re-examination.

The Royal Society of Chemistry apologises for these errors and any consequent inconvenience to authors and readers.

Acknowledgements

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References

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