

Supporting Information

Methylenation of Peptides by N,N,N,N-Tetramethylethylenediamine (TEMED)
under Conditions Used for Free Radical Polymerization: A Mechanistic Study

Mehrnoosh Shirangi,^{†,¶} Javier Sastre Toraño,[‡] Börje Sellergren,^{||} Wim E. Hennink,[†]
Govert W. Somsen,[‡] Cornelus F. van Nostrum^{*,†}

[†]Department of Pharmaceutics, Utrecht Institute for Pharmaceutical Sciences, Utrecht University, Utrecht, The Netherlands

[‡]Biomolecular Analysis, Utrecht Institute for Pharmaceutical Sciences, Utrecht University, Utrecht, The Netherlands

[¶]Current address: AIMMS Division of Biomolecular Analysis, VU University Amsterdam, Amsterdam, the Netherlands

[§] Institute of Environmental Research, Faculty of Chemistry, Technical University of Dortmund, Germany; current address: Department of Biomedical Sciences, Faculty of Health and Society, Malmö University, Sweden

^{||}Department of Drug and Food Control, Faculty of Pharmacy, Tehran University of Medical science, Tehran, Iran

*corresponding author: C.F.vanNostrum@uu.nl

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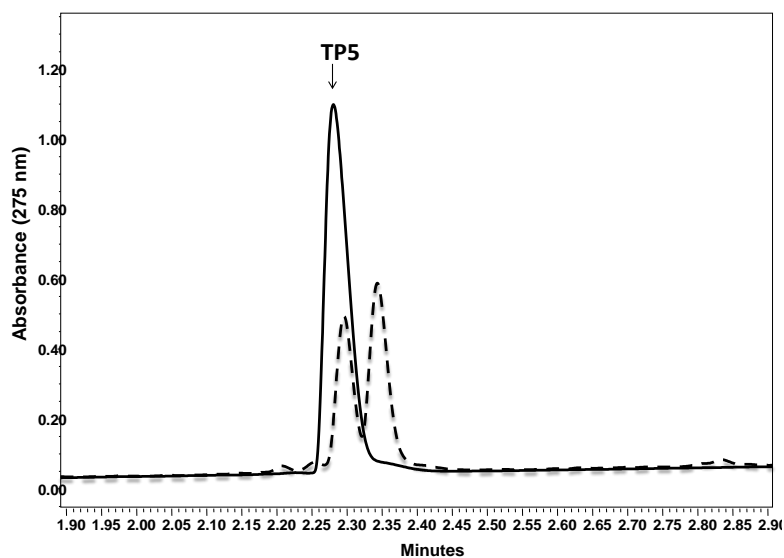


Figure S1. RP-UPLC chromatogram of native TP5 showing a single peak at 2.28 min (solid line), and extracted template after imprinting of TP5 in a polyacrylamide gel prepared by APS/TEMED at 50°C showing an additional degradation product at 2.36 min (dashed line).

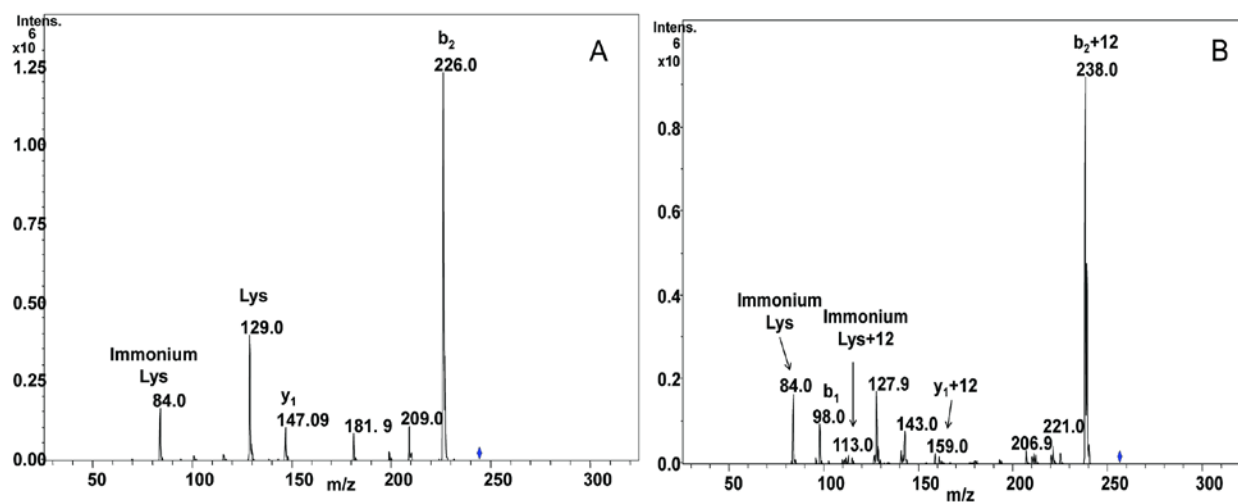


Figure S2. Tandem mass spectrum of dipeptide No.3 (Pro-Lys); (A) native, precursor ion at m/z 244.0, (B) modified, precursor ion at m/z 256.0.

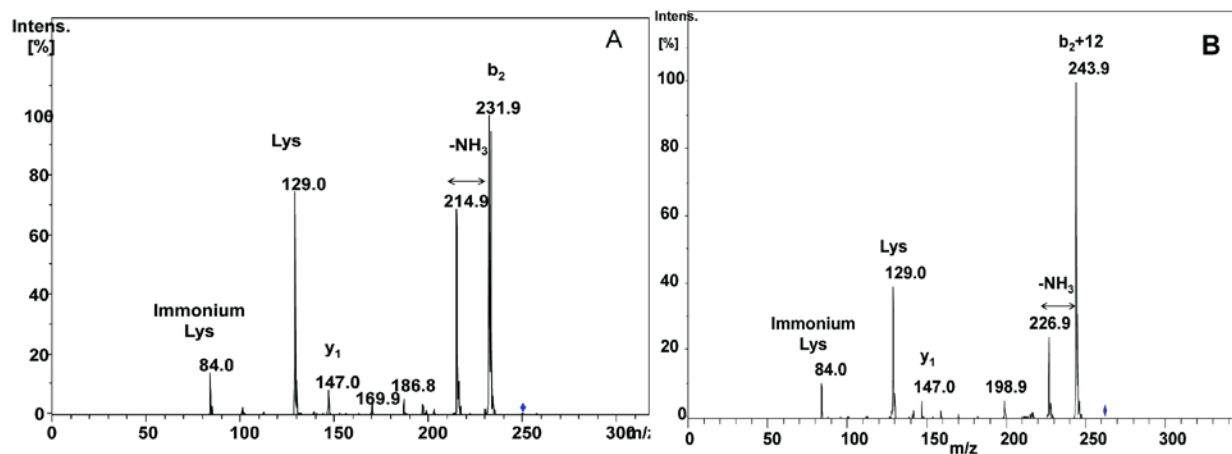


Figure S3. Tandem mass spectrum of dipeptide No.5 (Cys-Lys): (A) native, precursor ion at m/z 249.9, (B) modified, precursor ion, m/z 261.9.

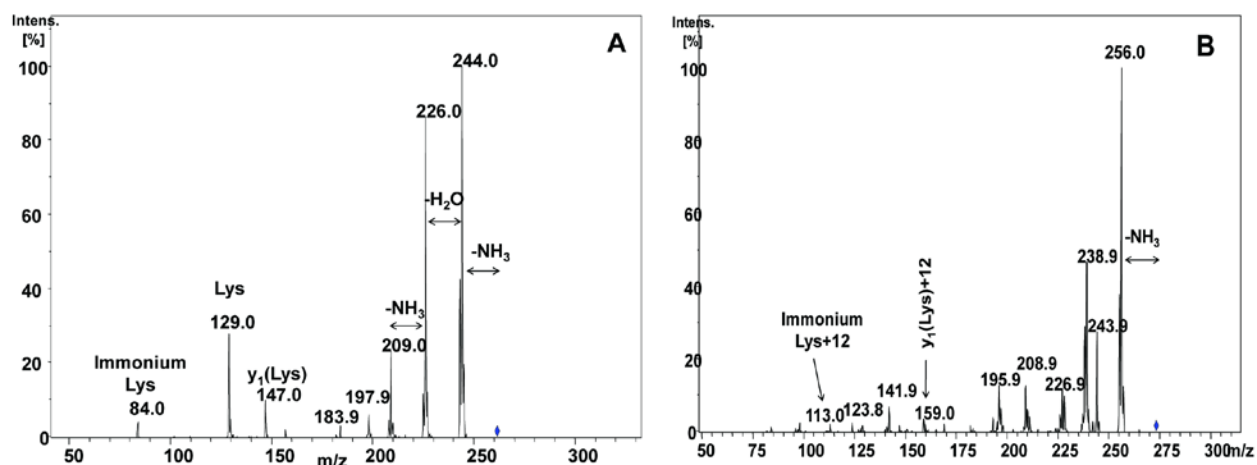


Figure S4. Tandem mass spectrum of dipeptide No.6 (Asn-Lys): (A) native, precursor ion at m/z 261.0, (B) modified, precursor ion at m/z 273.0

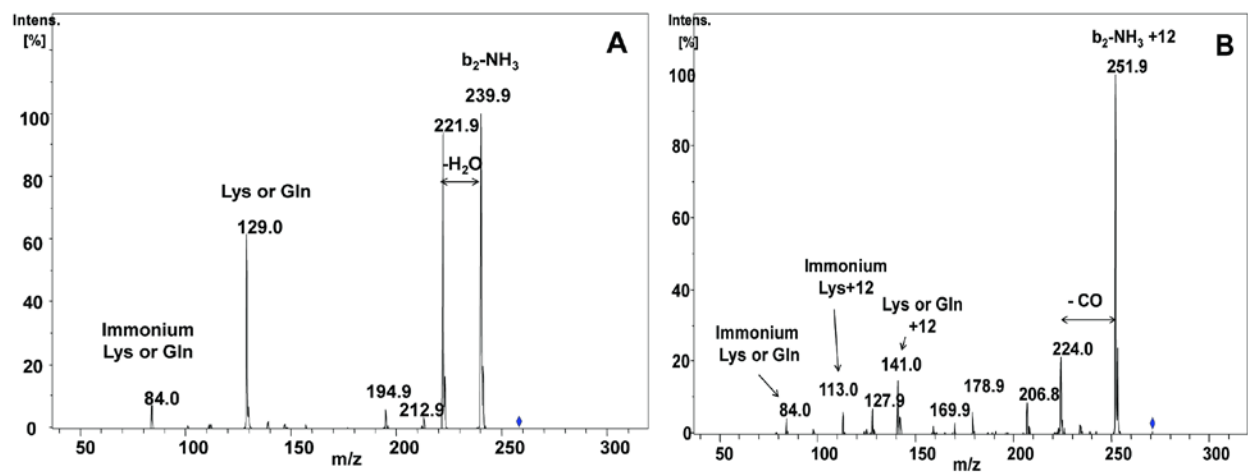


Figure S5. Tandem mass spectrum of dipeptide No.7 (Gln-Lys) -NH₃: (A) native, precursor ion at m/z 258.0, (B) modified, precursor ion at m/z 270.0

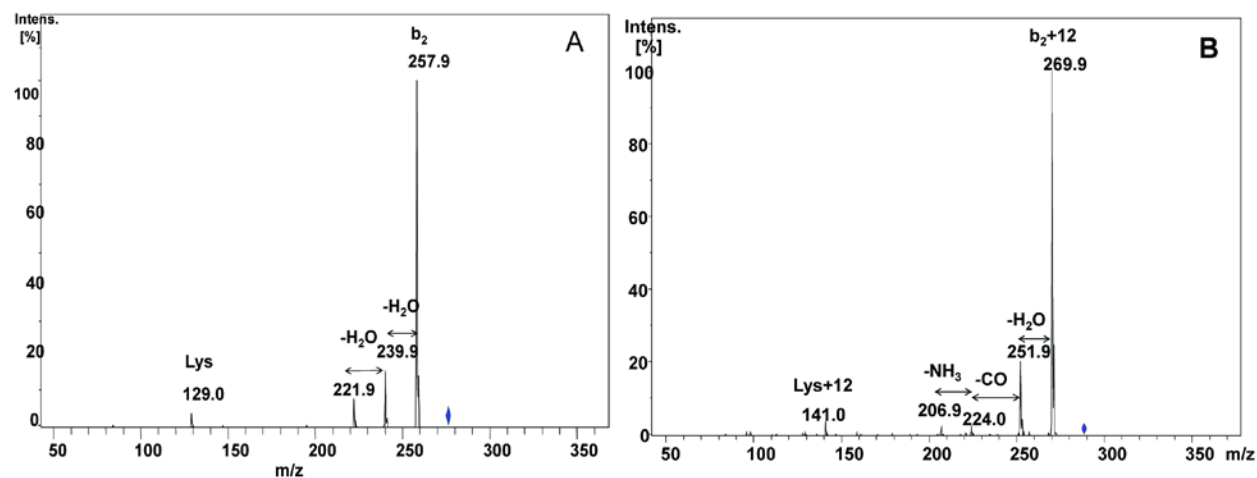


Figure S6. Tandem mass spectrum of dipeptide No.8 (Glu-Lys): (A) native, precursor ion at m/z 276.1, (B) modified, precursor ion at m/z 288.1.

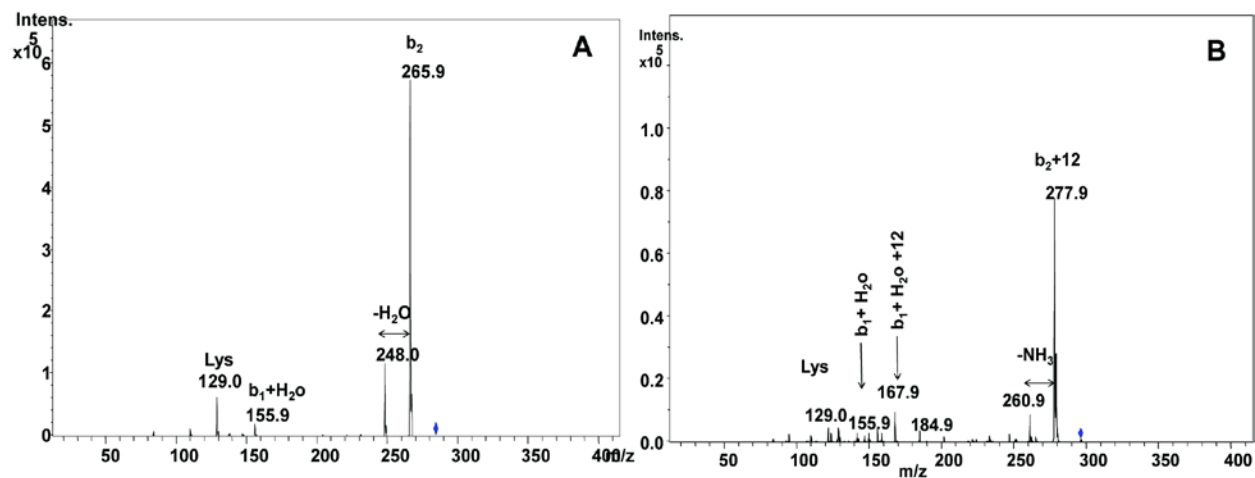


Figure S7. Tandem mass spectrum of dipeptide No.9 (His-Lys): (A) native, precursor ion at m/z 283.0, (B) modified, precursor ion at m/z 296.0.

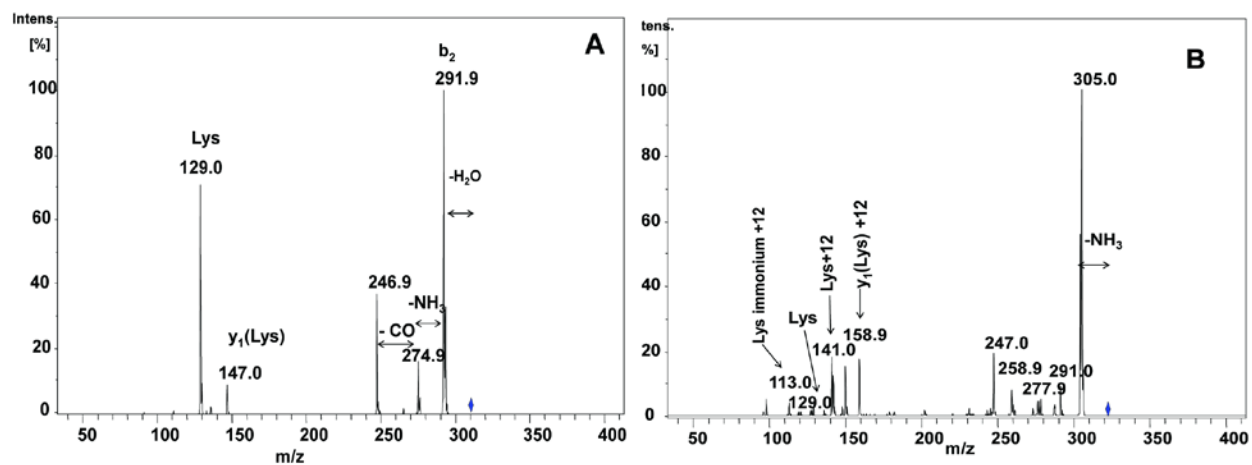


Figure S8. Tandem mass spectrum of dipeptide No.11 (Tyr-Lys): (A) native, precursor ion at m/z 310.0, (B) modified, precursor ion at m/z 322.0.

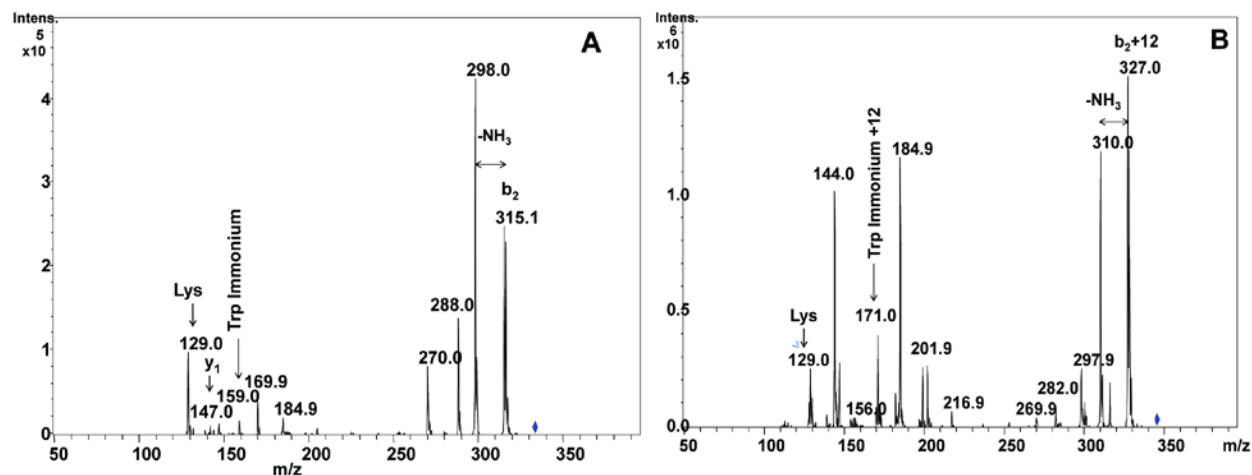


Figure S9. Tandem mass spectrum of dipeptide No.12 (Trp-Lys): (A) native, precursor ion at m/z 333.0, (B) modified, precursor ion at m/z 345.0.

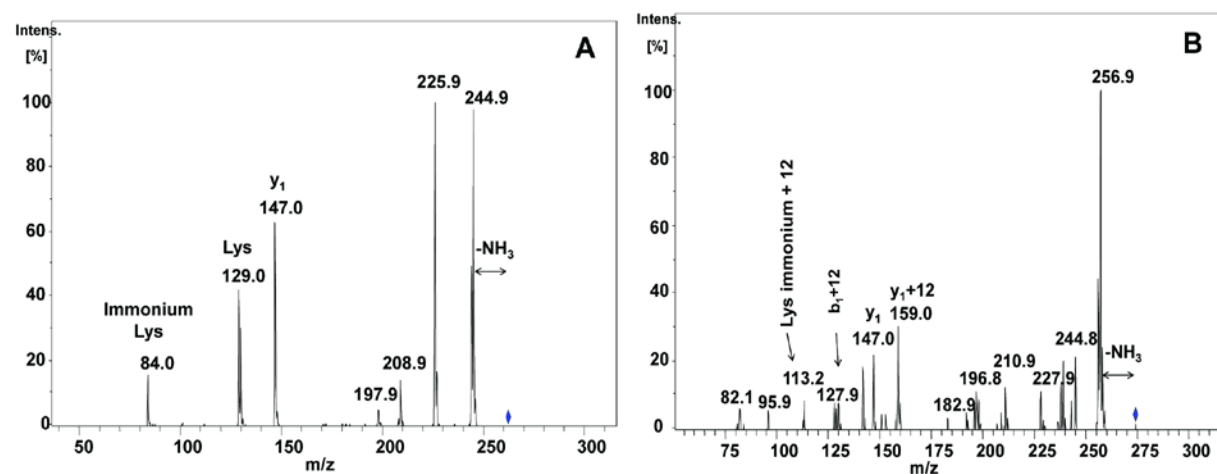


Figure S10. Tandem mass spectrum of dipeptide No.14 (Asp-Lys): (A) native, precursor ion at m/z 262.0, (B) modified, precursor ion at m/z 274.0.

Table S1: Accurate mass measurements of thymopentin and its modified product

| Name | Molecular formula | Observed m/z | Calculated m/z | Error (mDa) |
|-------------------------|----------------------------|-------------------|---------------------|-------------|
| Thymopentin | $[C_{30}H_{49}N_9O_9+H]^+$ | 680.3726 | 680.3726 | 0.0 |
| Modified thymopentin | $[C_{31}H_{49}N_9O_9+H]^+$ | 692.3734 | 692.3726 | -0.8 |