

Supporting Information

Femtosecond laser-induced scratch ablation as an efficient new method to evaluate the self-healing behavior of supramolecular polymers

Marcus Abend, Clemens Kunz, Steffi Stumpf, Stephan Gräf, Stefan Zechel, Frank A. Müller, Martin D. Hager and Ulrich S. Schubert**

M. Abend, S. Stumpf, Dr. S. Zechel, Dr. M. D. Hager, Prof. Dr. U. S. Schubert

Laboratory of Organic and Macromolecular Chemistry (IOMC)

Friedrich Schiller University Jena, Humboldtstr. 10, 07743 Jena (Germany)

*E-mail: ulrich.schubert@uni-jena.de; www.schubert-group.de

*E-mail: martin.hager@uni-jena.de; www.schubert-group.de

M. Abend, S. Stumpf, Dr. S. Zechel, Prof. Dr. F. A. Müller, Dr. M. D. Hager, Prof. Dr. U. S. Schubert

Jena Center of Soft Matter (JCSM)

Friedrich Schiller University Jena, Philosophenweg 7, 07743 Jena (Germany)

C. Kunz, Dr. S. Gräf, Prof. Dr. F. A. Müller

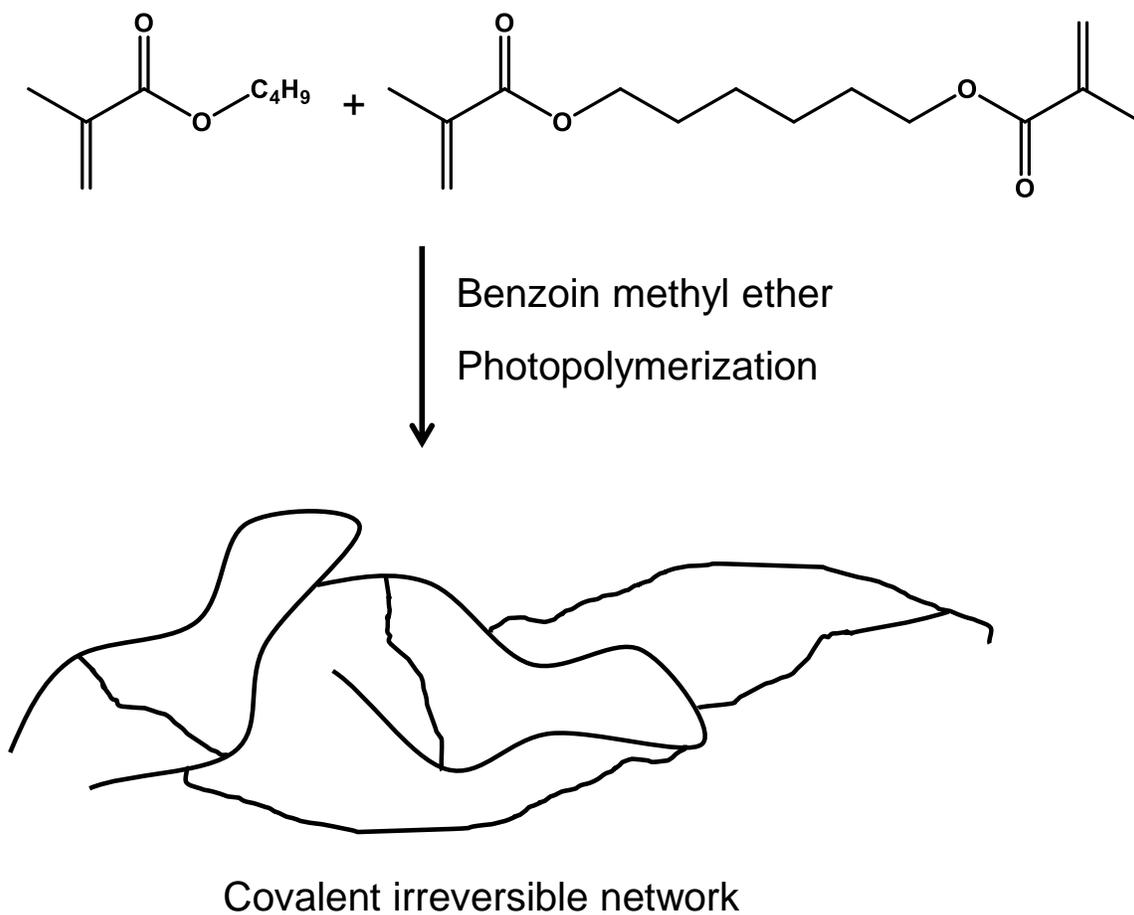
Otto Schott Institute of Materials Research

Friedrich Schiller University Jena, Löbdergraben 32, 07743 Jena (Germany)

Experimental section:

All polymer syntheses were performed according to Bode *et al.*^[31]

Schemes figures and tables:



Scheme S1: Schematic representation of the synthesis of the reference samples **S_R**.

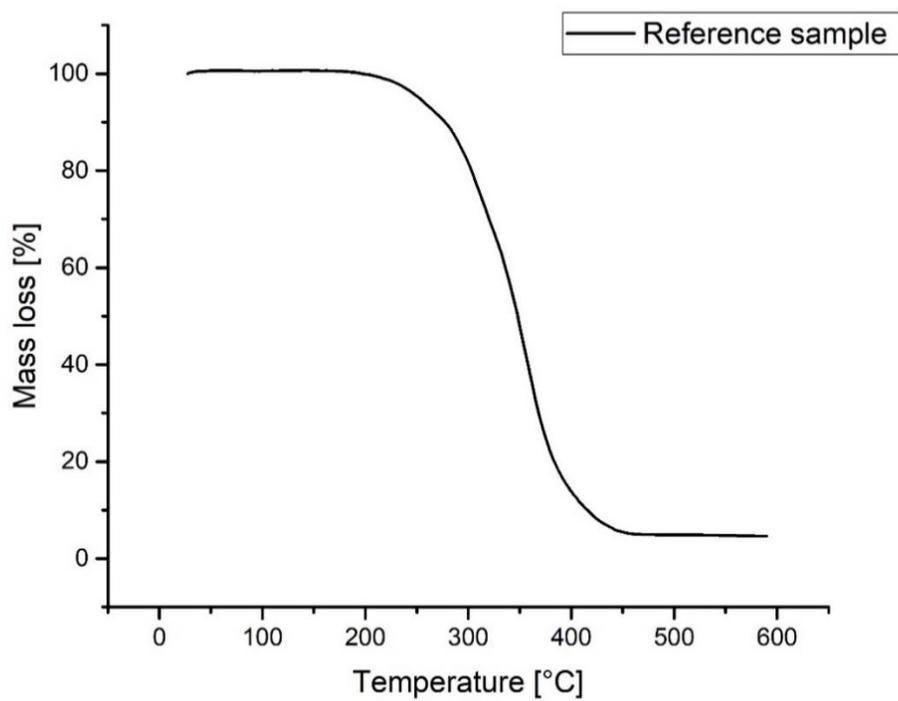
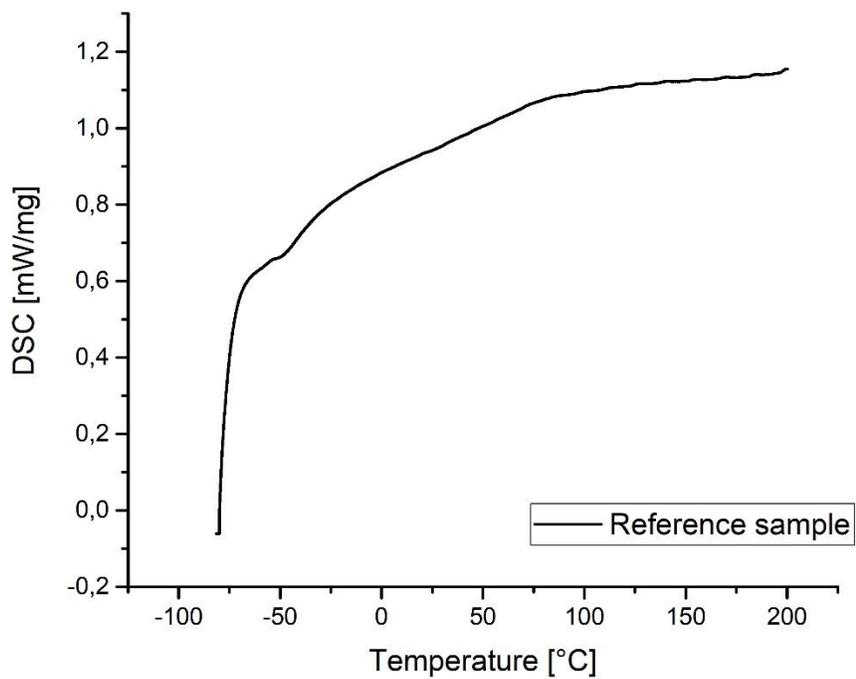


Figure S1: DSC curves (2nd heating) and TGA of the reference sample.

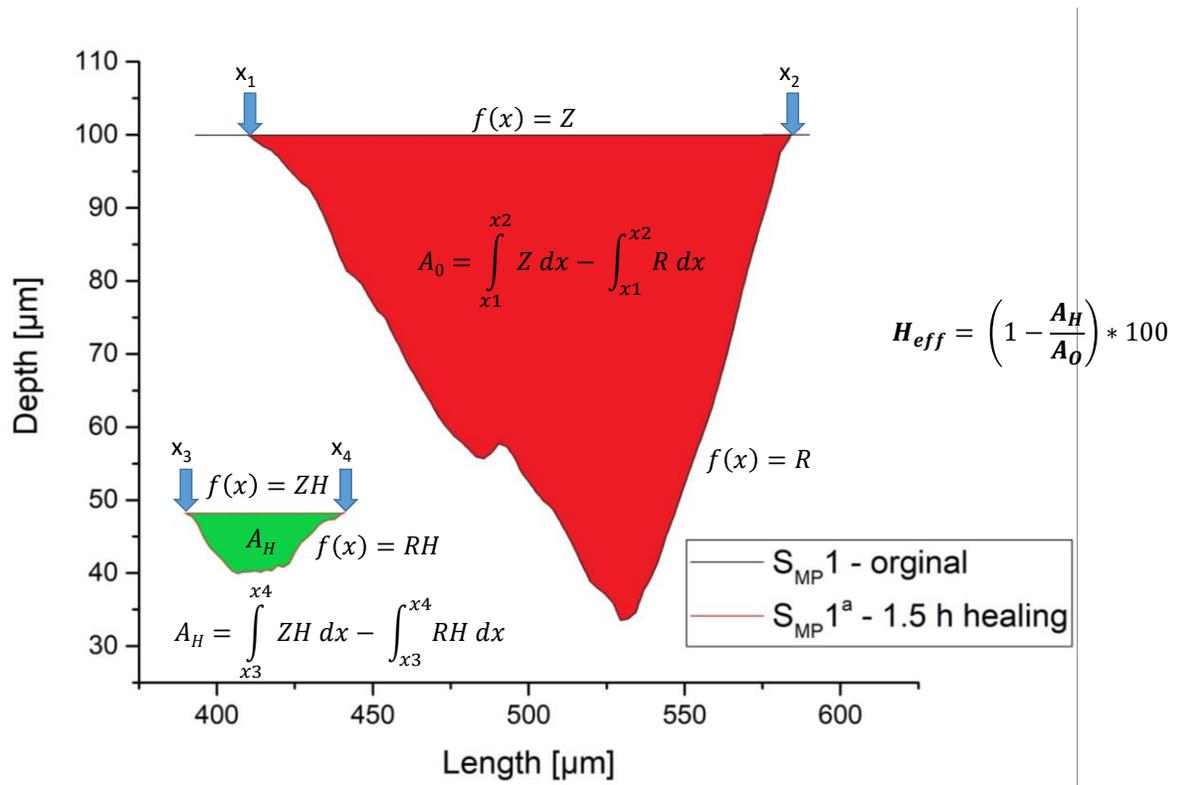


Figure S2: Schematic representation of the calculation of A_0 . Integration of the areas below the zero line and the curve. Simple subtraction results in the profile area.



Figure S3: Crack made with a scalpel induced into the metallopolymer based on poly(butyl methacrylate) crosslinked via manganese(II)-chloride-terpyridine interactions. Cracks and ridges can be seen on the crack edge.

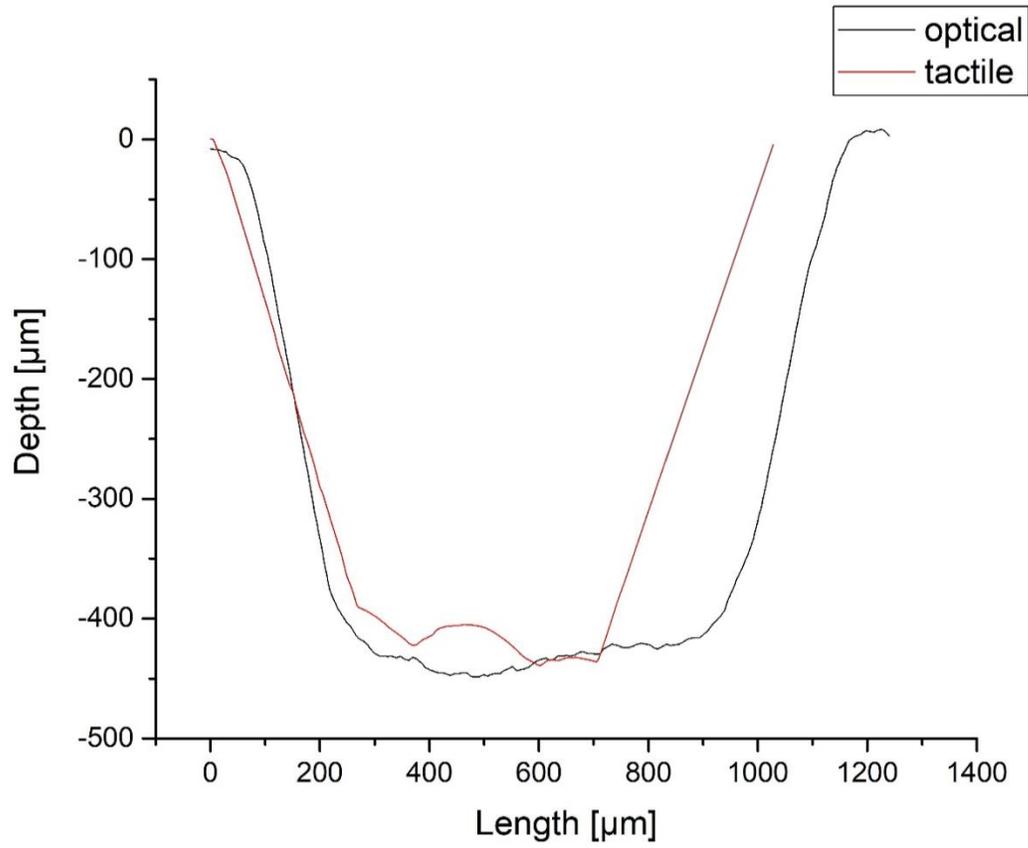


Figure S4: Comparison of optical and tactile measurement of a defect in the metallopolymer.

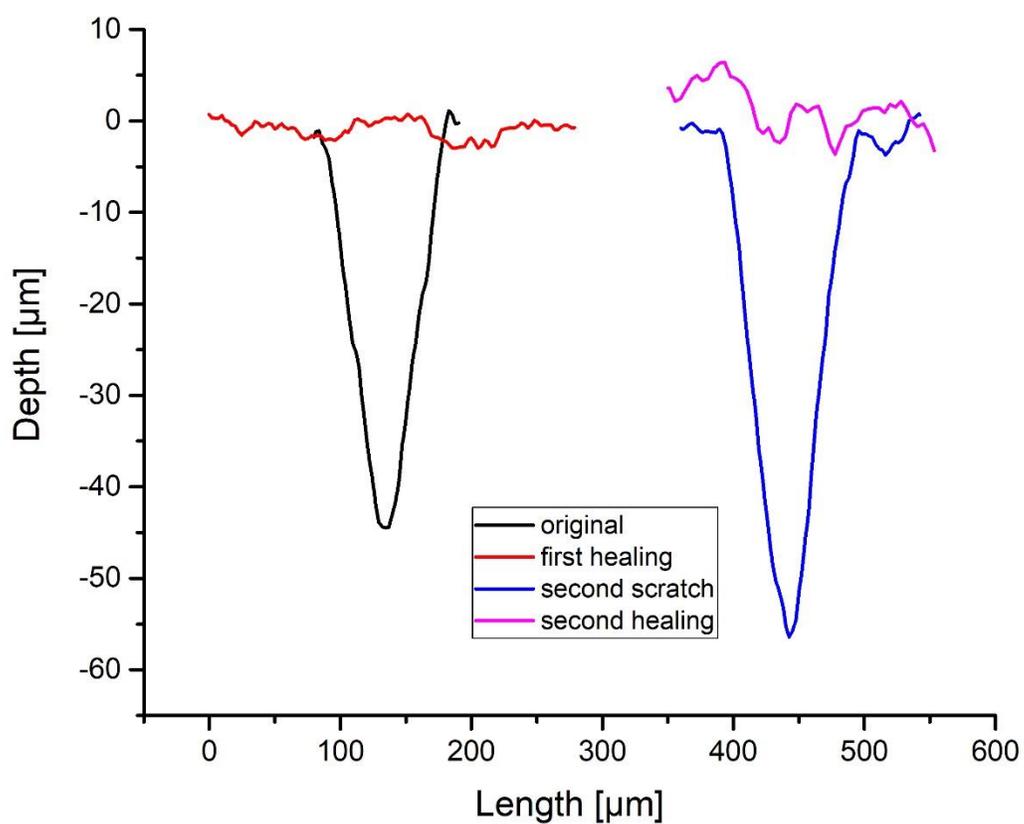
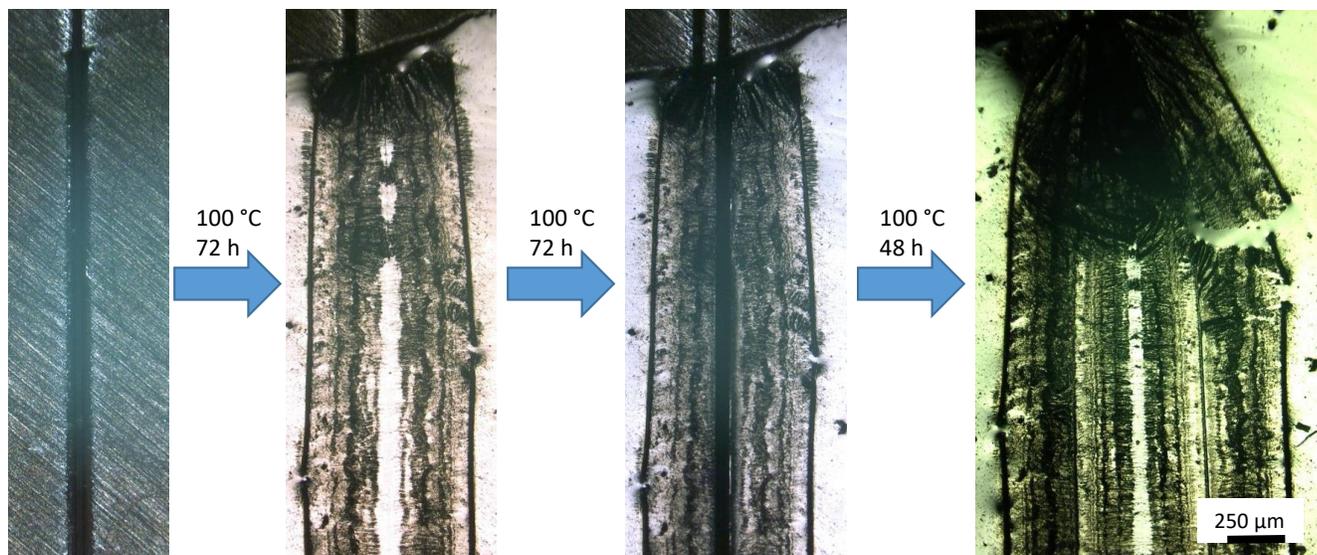


Figure S5: Comparison of multiple healing, left side: first healing, right side: second healing.

The polymer was processed with the same laser parameter as for sample **SMP3**.

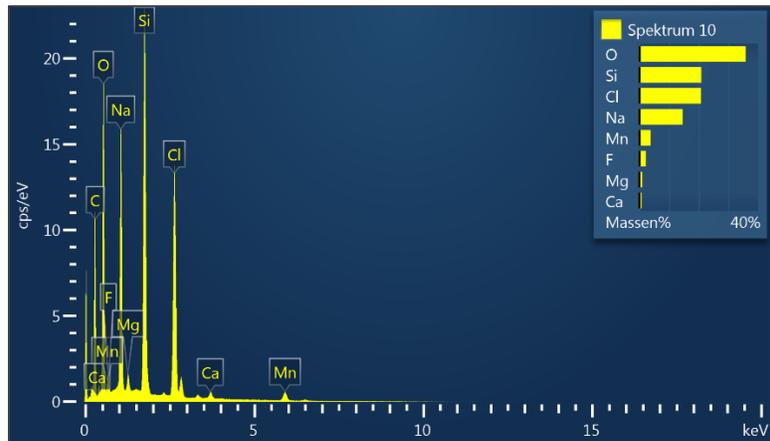


Figure S6: EDX measurement at area C of the scratch **Smp4**; due to the high laser intensity the polymer and even the glass were sublimated. Components of the glass can be detected on the surface.

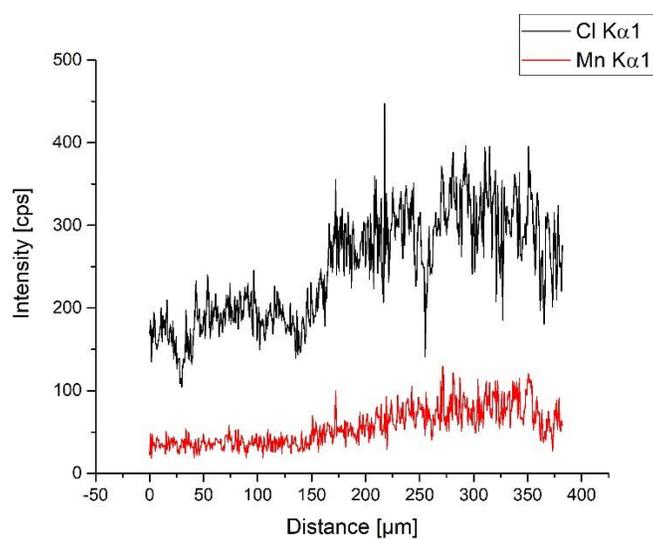
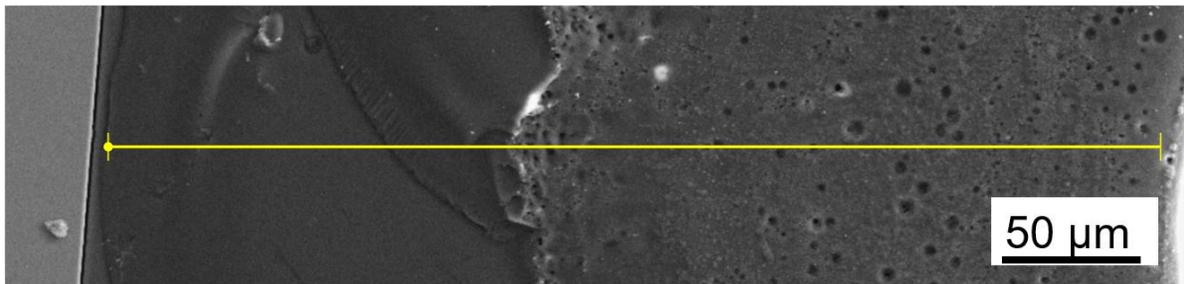


Figure S7: Line scan sample **SMP4** from point A to B. A higher amount of manganese in the sublimated polymer range was found.

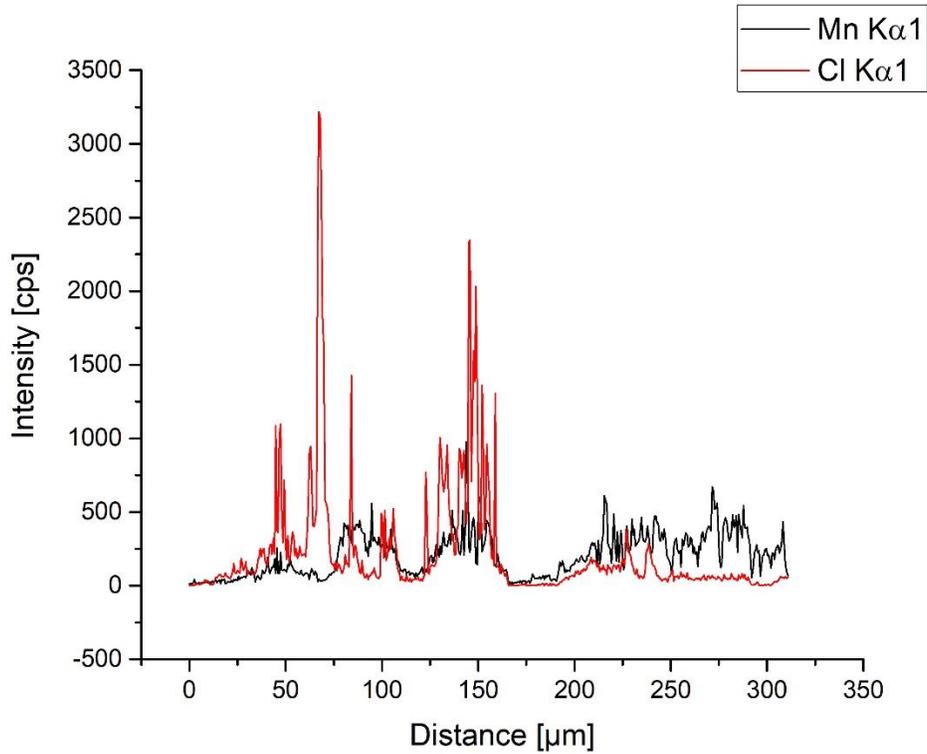
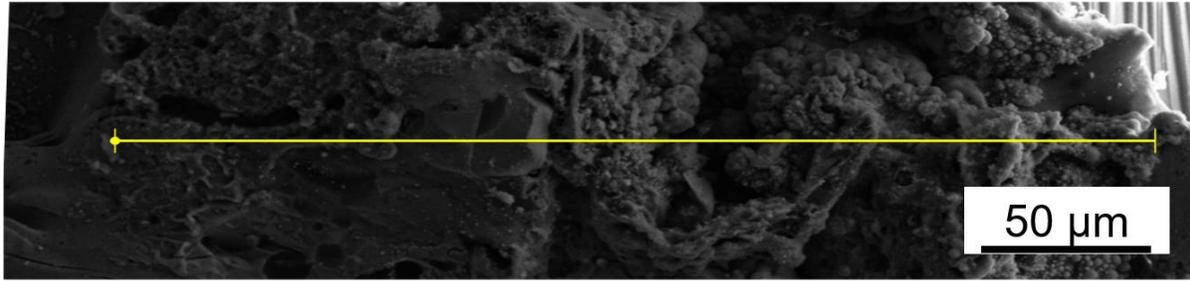


Figure S8: Line scan of sample **SMP4** from point C to D. The complexing agent is distributed irregularly. The intensive laser radiation has destroyed the surface.

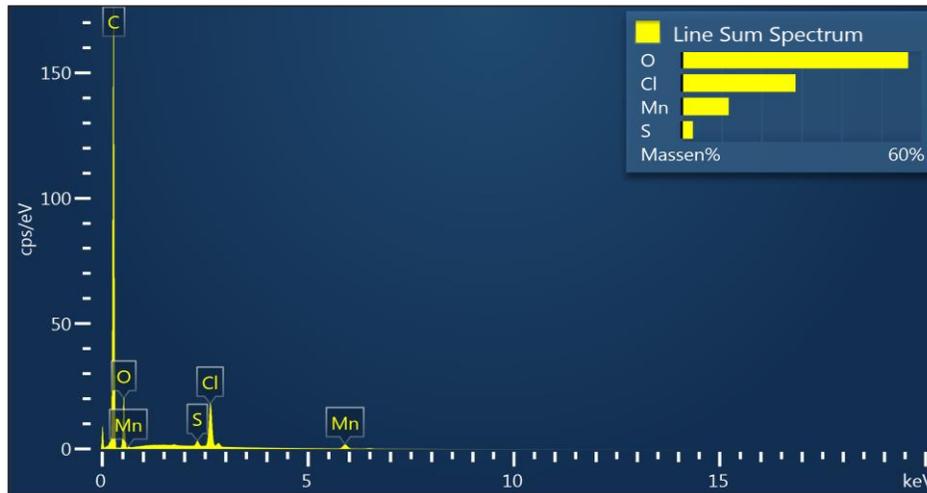
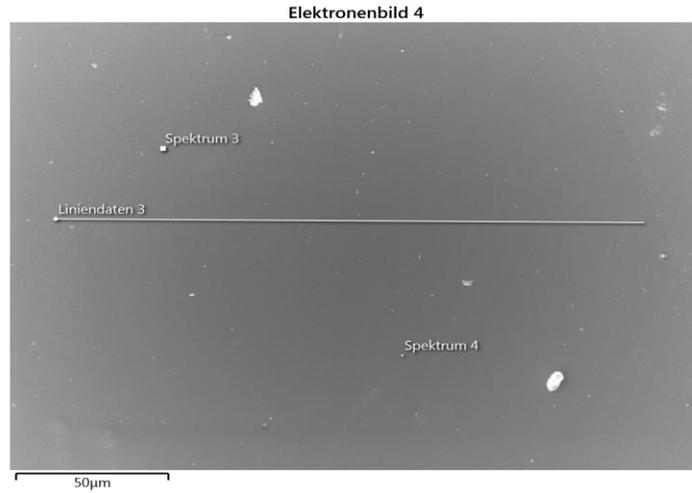


Figure S9: Line sum spectrum of EDX measurement at the polymer surface before healing.

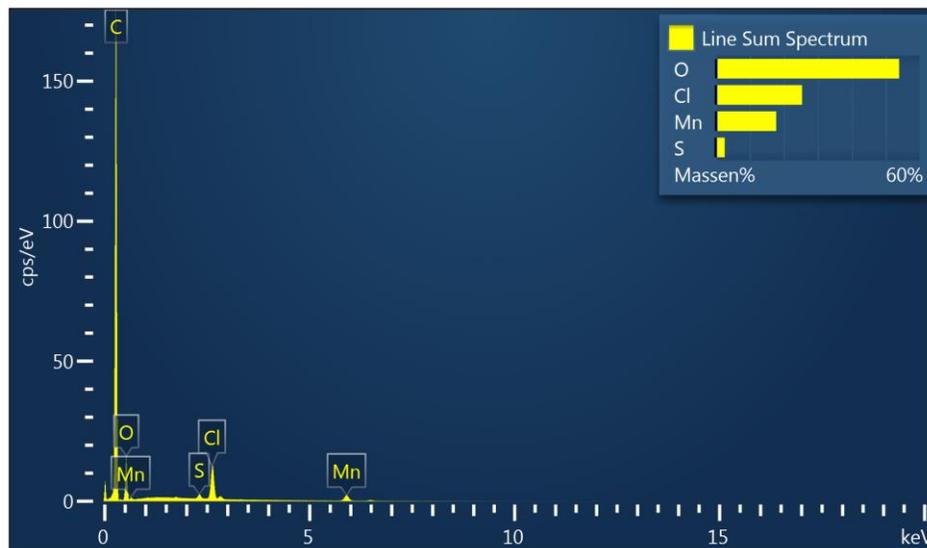
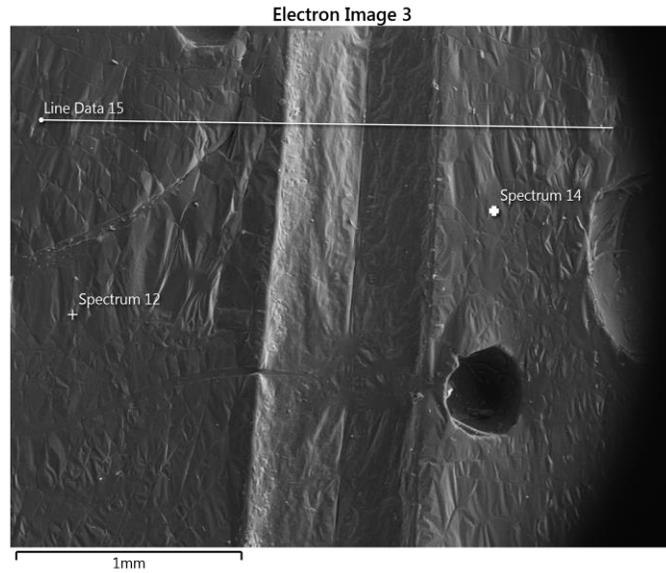


Figure S10: Line sum spectrum of EDX measurement at the polymer surface after healing. The polymer was processed with the same laser parameter as for sample **SMP3**.

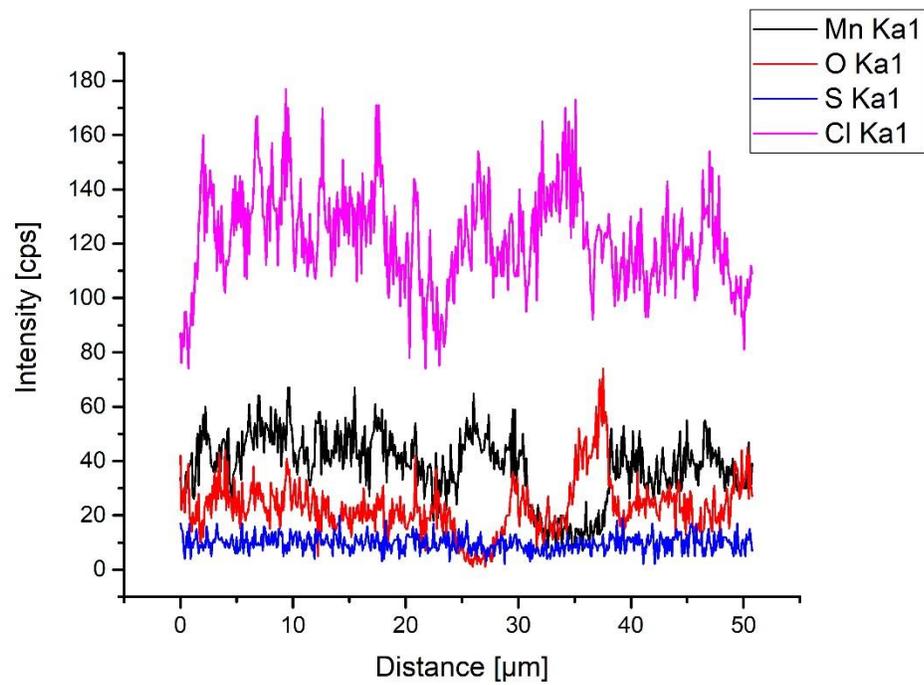
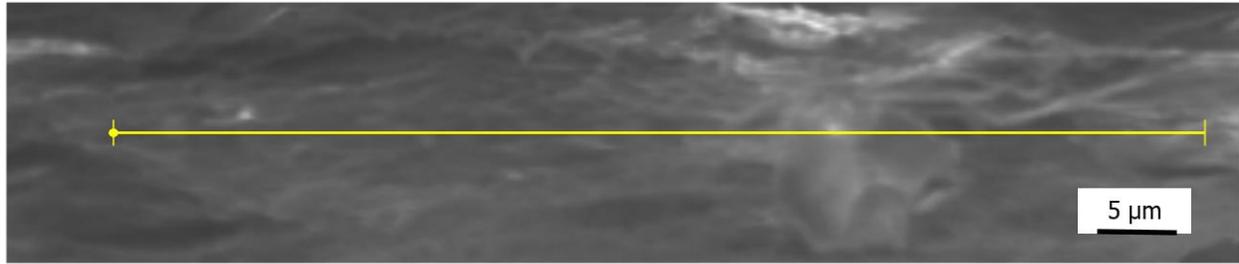


Figure S11: Line scan of a metallopolymer at a scratch flank before healing. The present elements are equally distributed. The polymer was processed with the same laser parameter as for sample **S_{MP3}**.

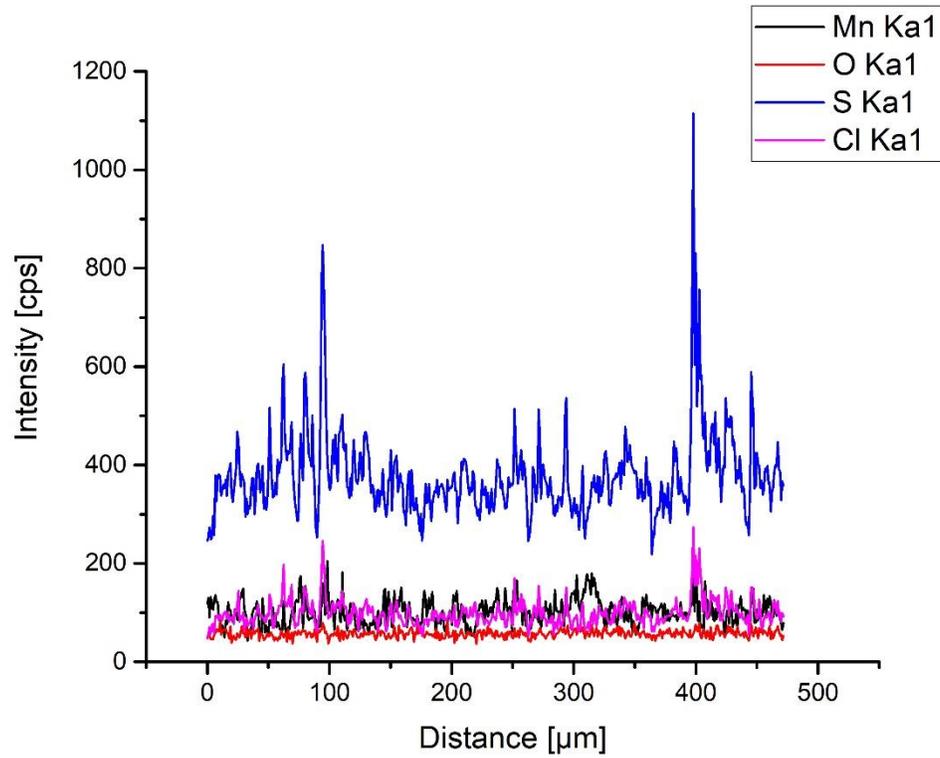
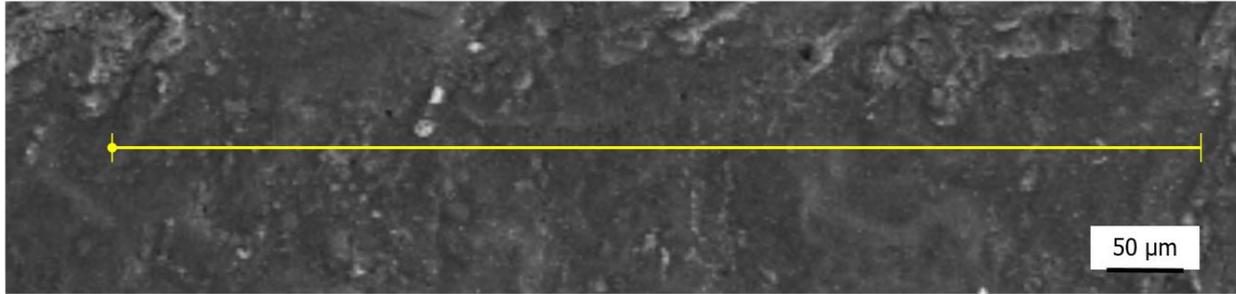
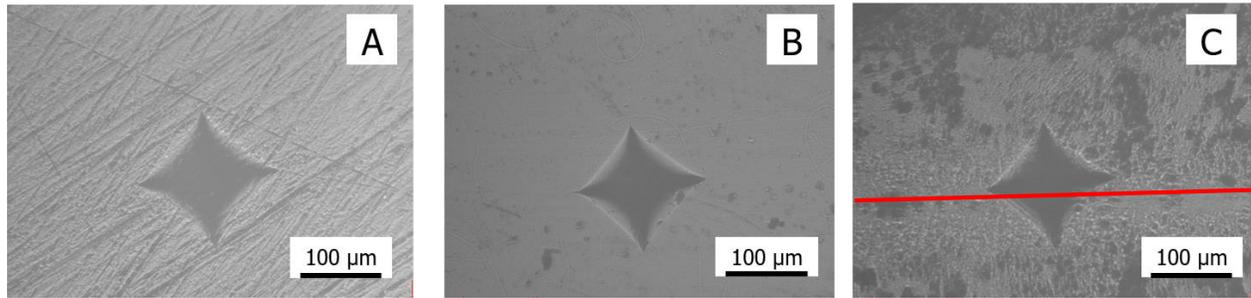


Figure S12: Line scan of a metallopolymer at a scratch flank after healing. The present elements are equally distributed. The polymer was processed with the same laser parameter as for sample **SMP3**.



Reference, next to the scratch (A)		Healed scratch	
Left side	Right side	Next to scratch (B)	In scratch (C)
5.2 HV 0.1/30	5.1 HV 0.1/30	6.2 HV 0.1/30	6.2 HV 0.1/30

Figure S13: Hardness test according to Vickers with a load of 0.1 N and a load duration of 30 seconds. Figure A and Figure B show measurements near to the scratch before and after healing. Figure C shows a measurement in scratch area after healing. The red line indicates the center of the healed scratch.