Supporting Information

Thermally Responsive Core-shell Microparticles and Cross-linked Networks Based on Nitrone Chemistry

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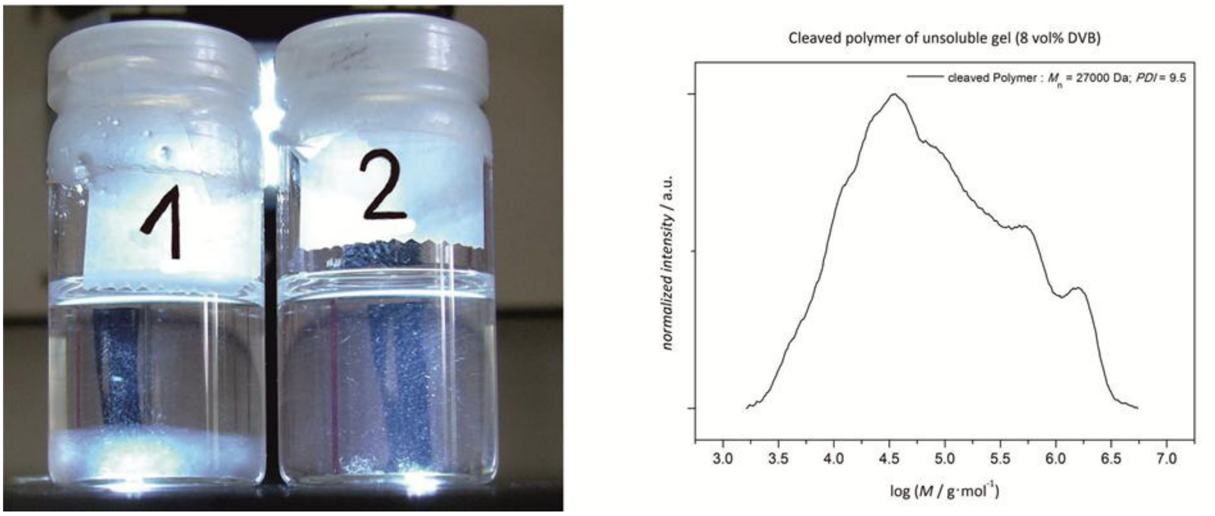
Cleavage of ESCP Generated Unsoluable Networks

After cleavage, performed at 125 °C with a large excess of TEMPO overnight, the resulting network fragments were fully soluble in THF, allowing SEC analysis and demonstrating the large range and efficiency of the cleavage reaction (Figure S1).



FigureS1: Photographic comparison of THF solubility of 8 vol% DVB gel before (**1**) and after (**2**) cleavage (left) and SEC analysis of the cleaved product (M_n = 27 000 g·mol^{-1}; PDI = 9.5) (right).

Network Formation and Cleavage into Linear Chains

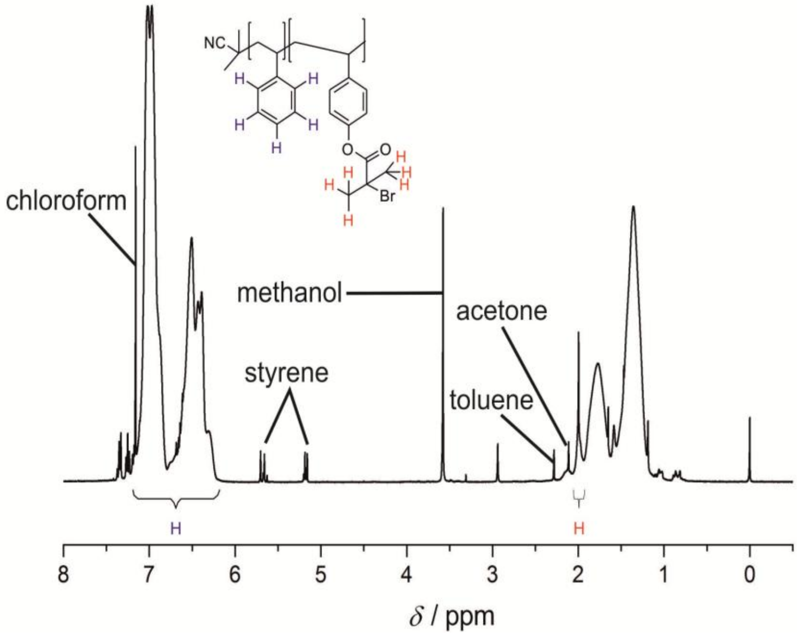


Figure S2:^{1}H NMR spectrum of a copolymer containing styrene and VBMP. Protons of different organic small molecules present during the synthesis are also visible in the spectrum.

In order to determine the degree of bromine functionality per polymer chain, NMR samples were taken from polymers synthesized with different amounts of VBMP. For each sample the integral of the signal between 6.2-7.2 ppm assigned to the aromatic protons ($C_6\mathbf{H}_5$) of the styrene monomer was compared to the integral of the singlet signal of the methyl protons of the VBMP comonomer at 2.0 ppm. Because the aromatic protons of the VBMP comonomerare also included in the styrene integral, the integralof the methyl protons was set to a value of 6 and a value of 4 was subtracted from the aromatic proton integral.Integrals were then divided by the number of the protons within the respective functionality and set into relation to calculate the incorporation of VBMP. The number of bromine functions correlates with the number of incorporated VBMP comonomer, as every VBMP comonomer contains one bromine function. As the vinyl group in styrene and VBMP is assumed to be similar in reactivity, the number of bromine functionality per chain can also be estimated in a second way, by assuming unity for the copolymerization parameters, leading to statistical incorporation of comonomer and a ratio of incorporated monomers identical to the monomer feed.The obtained data, however, show that the NMR analysis suggests a higher number of bromine atoms per single chain than the assumption of an ideal copolymerization. The difference could be due to the fact that the NMR data overestimates the number of bromine atoms due to the fact that the single peak of the two CH_3 groups is overlapping with the polymer backbone proton signals.

Synthesis of Poly(Divinyl Benzene) Microspheres Employing Nitrone Chemistry

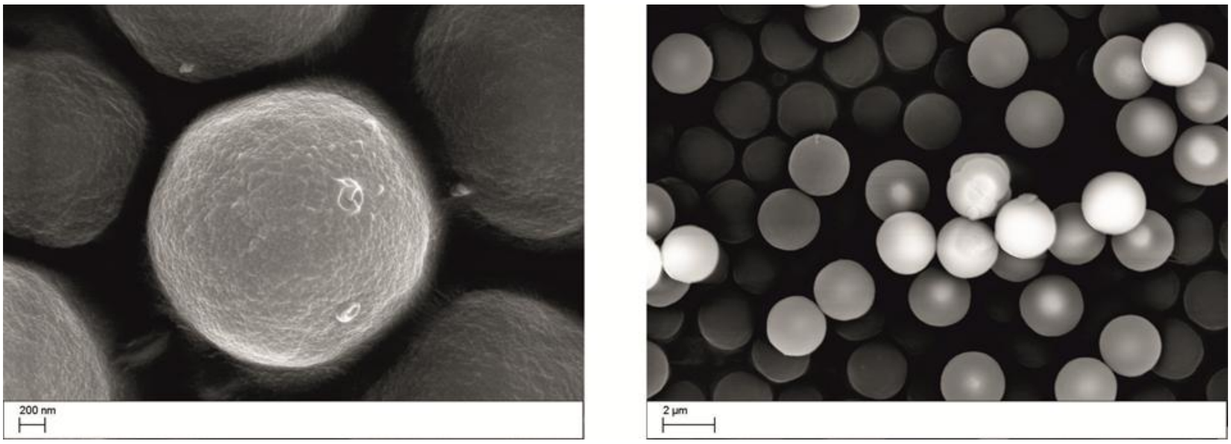


Figure S3: Scanning electron microscopy (SEM) images of microspheres synthesized via distillation precipitation polymerization with addition of 4.3 wt% PBN (microsphere 1), showing monodisperse microspheres with a smooth surface.

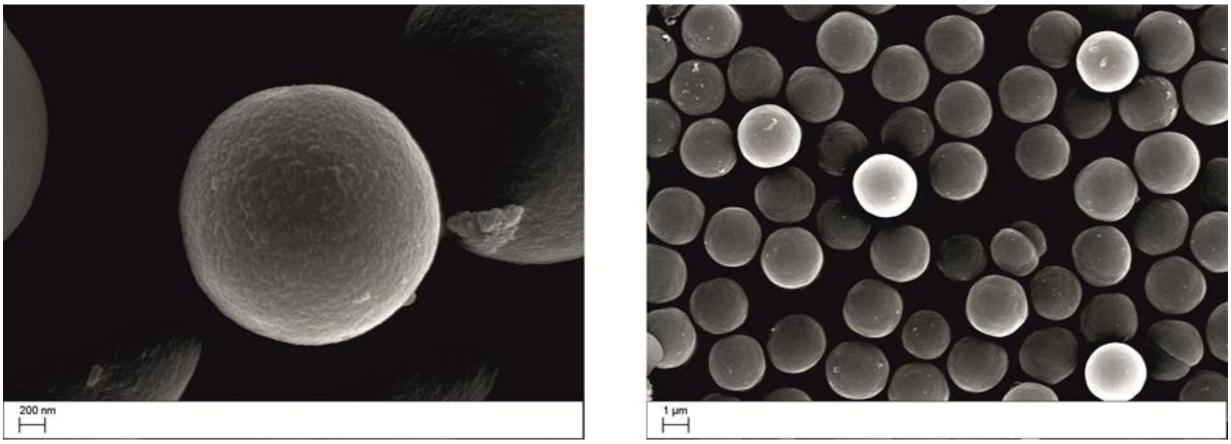


Figure S4: Scanning electron microscopy (SEM) images of microspheres synthesized via distillation precipitation polymerization with addition of 8.6 wt% PBN (microsphere 2), showing monodisperse microspheres with a smooth surface.

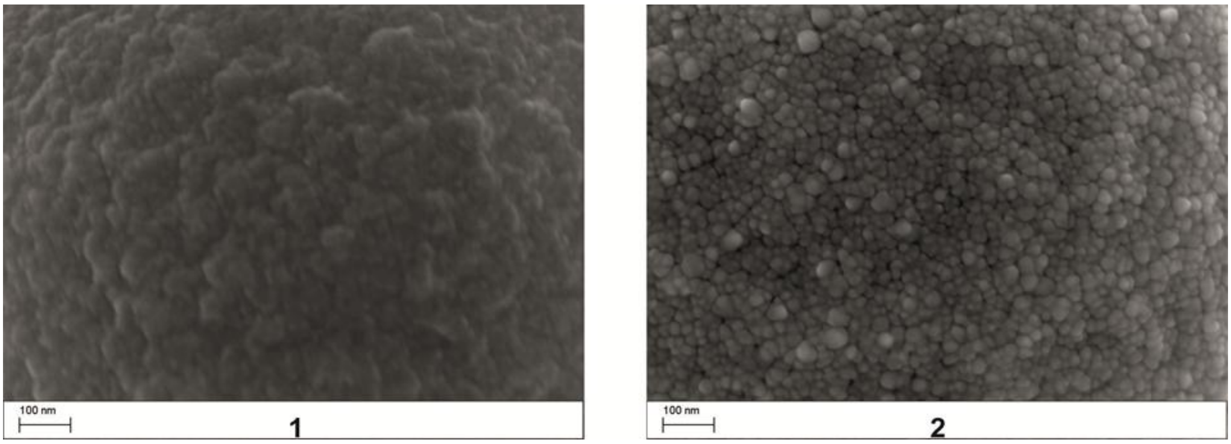


Figure S5: Close-up view of the microsphere surfaces before (1) and after (2) the nitroxide mediated polymerization. The smooth surface of the original microsphere becomes substantially rougher. The small exaltations are an indication for formed polymeric ‘loops’.