Electronic Supplementary Material (ESI) for Polymer Chemistry.

—Supporting Information—

Two in One: Use of Azide Functionality for Controlled Photo-crosslinking and Click-modification of Polymer Microspheres

Marco Albuszis,[†] Peter. J. Roth,[‡,] Werner Pauer,[†,]* and Hans-Ulrich Moritz[†,]**

[†] Institute for Technical and Macromolecular Chemistry, University of Hamburg, Bundesstraße 45, 20146 Hamburg, Germany

[‡] Department of Chemistry, Faculty of Engineering and Physical Sciences, University of Surrey, Guildford, Surrey, GU2 7XH, United Kingdom

Corresponding Author Email Addresses:

P. J. Roth (p.roth@surrey.ac.uk)

W. Pauer (pauer@chemie.uni-hamburg.de)

H.-U. Moritz (moritzhu@chemie.uni-hamburg.de)

Synthesis of Chloromethyl-functional Microspheres

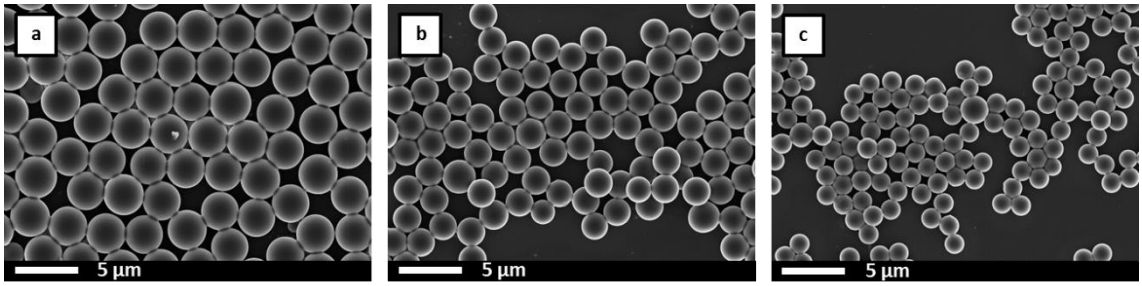

Figure S1. SEM images of 4-vinylbenzyl chloride (VBC)-functional microspheres with VBC feed contents of (a) 10 wt-%; (b) 50 wt-%; (c) 100 wt-% showing well-defined microspheres.

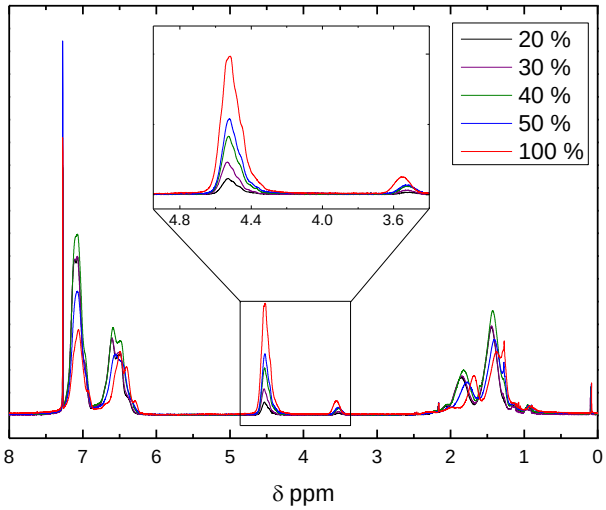

Figure S2. ^{1}H NMR spectra of microspheres (dissolved in $CDCl_3$) containing 4-vinylbenzyl chloride in varying amounts (20, 30, 40, 50, 100 wt-%). δ/ppm = 7.30–6.20 (Ar–*H*); 4.51 (–C*H*$_2$Cl); 3.51 (–C*H*$_2$OEt); 2.10–0.90 (backbone).

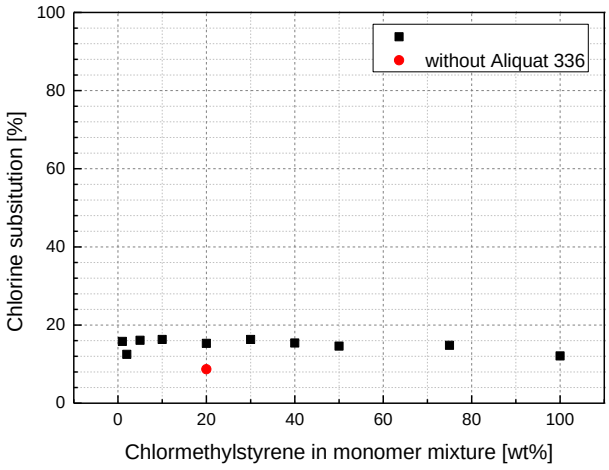

Figure S3. Degree of chlorine substitution by ethanol for different 4-vinylbenzyl chloride contents in poly(styrene-*co*-4-vinylbenzyl chloride) microspheres.

Azidomethyl-functional Microsphere Characterization

Figure S4. Photographs of microsphere samples MS_1 (left), MS_{50} (middle), and MS_{100} (right) showing powders of white to yellow color depending on VBA content.

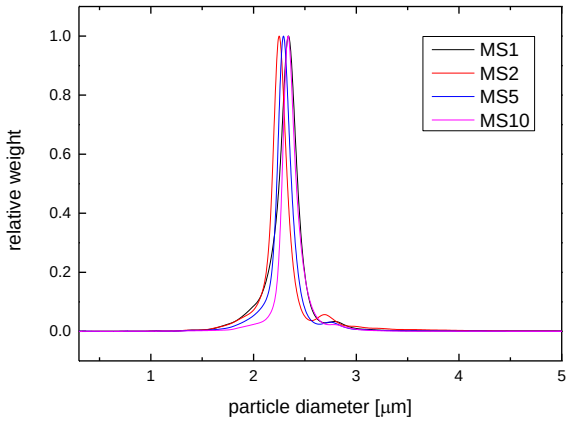

Figure S5. Disc centrifuge results of samples MS_1 (black), MS_2 (red), MS_5 (blue), and MS_{10} (pink) giving particle diameters around 2.5 µm.

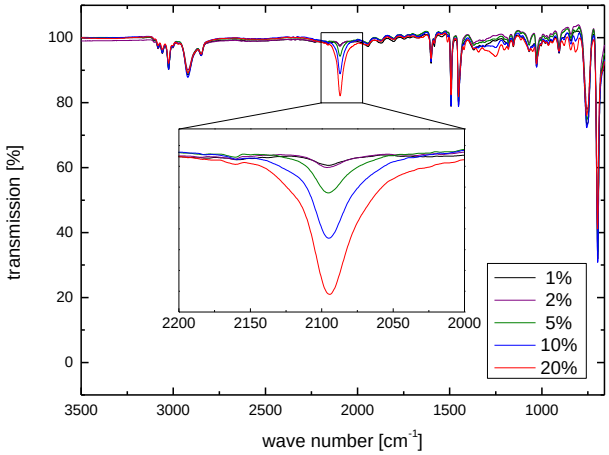

Figure S6. IR spectra of P(S-*co*-VBA) microspheres with VBA feed ranging from 1–20 wt-% with the N=N=N asymmetric stretch band inset

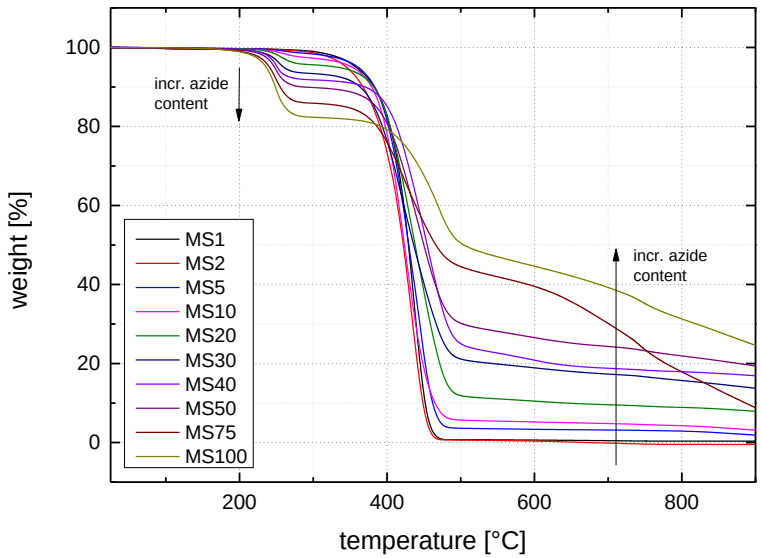

Figure S7. Thermogravimetric analysis of azide-functional microspheres showing the azide-to-nitrene reaction around 250 °C and the decomposition of the polymer material as of ~ 350 °C.

Photo-crosslinking

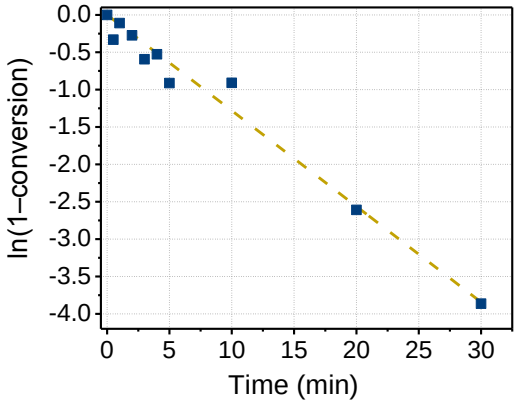

Figure S8. First order kinetic fit of the IR-determined azide conversion during the irradiation of sample MS_{100}.

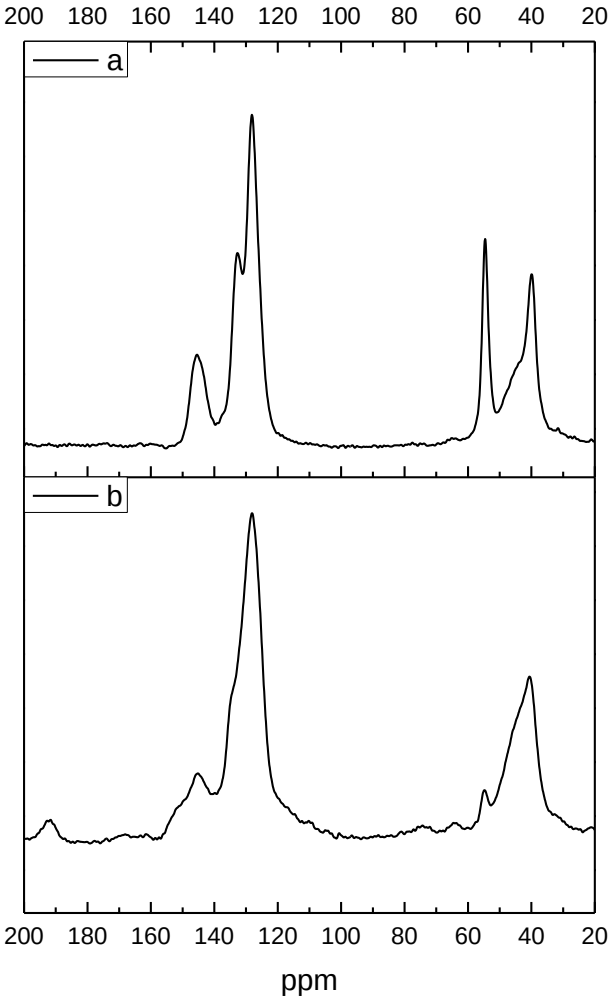

Figure S9. ^{13}C solid state NMR spectra of microspheres MS_{100} before (top) and after (bottom) exhaustive photo-crosslinking.