Hyperbranched PIBs for Self-Healing Polymers

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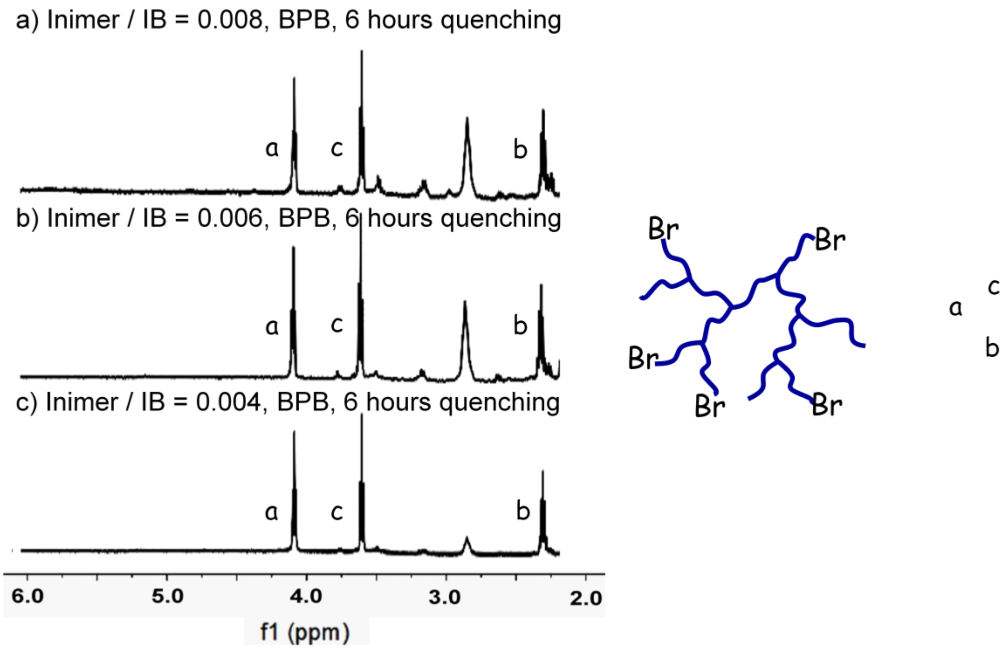
Supporting information

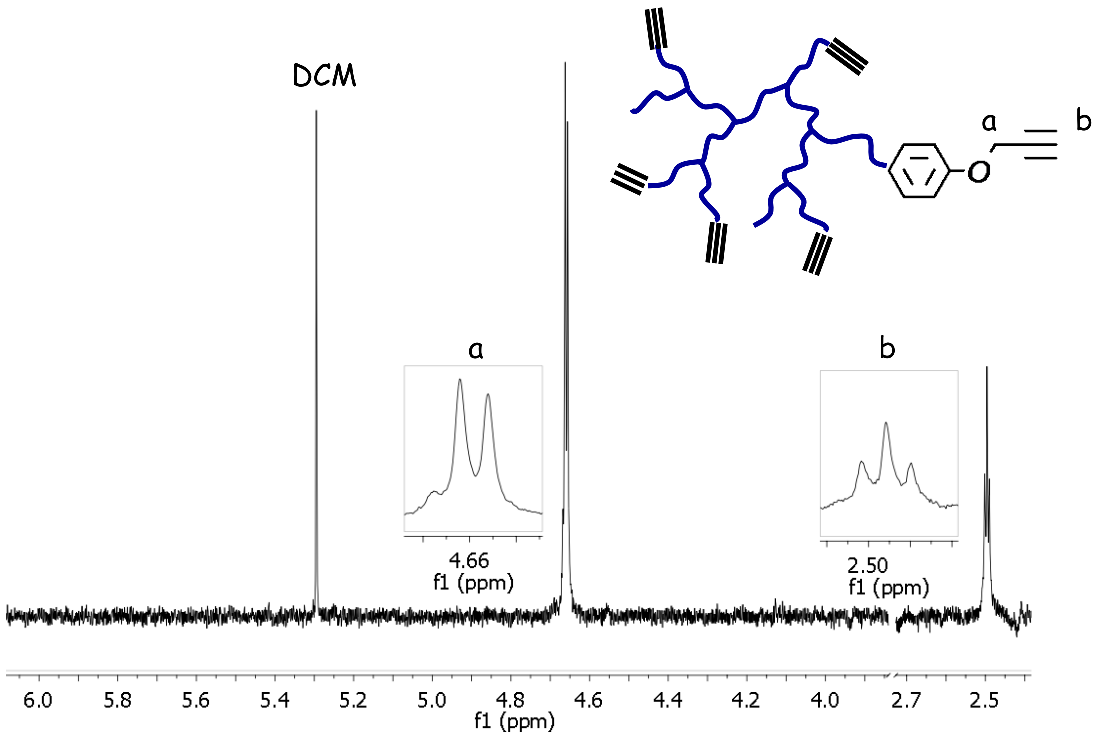
1. Characterization

S1 Analysis of endgroup distribution of hyperbranched PIBs via [1]H-NMR-spectroscopy after 6 hours quenching with BPB (26 equ. of inimer) followed by ATMS (26 equ. with respect to inimer) applying different inimer to isobutylene ratios. IM / IB = 0.008: a) Inimer / IB = 0.008, BPB and ATMS, 6 hours quenching, b) Inimer / IB = 0.006, BPB and ATMS, 6 hours quenching, c) Inimer / IB = 0.004, BPB and ATMS, 6 hours quenching.

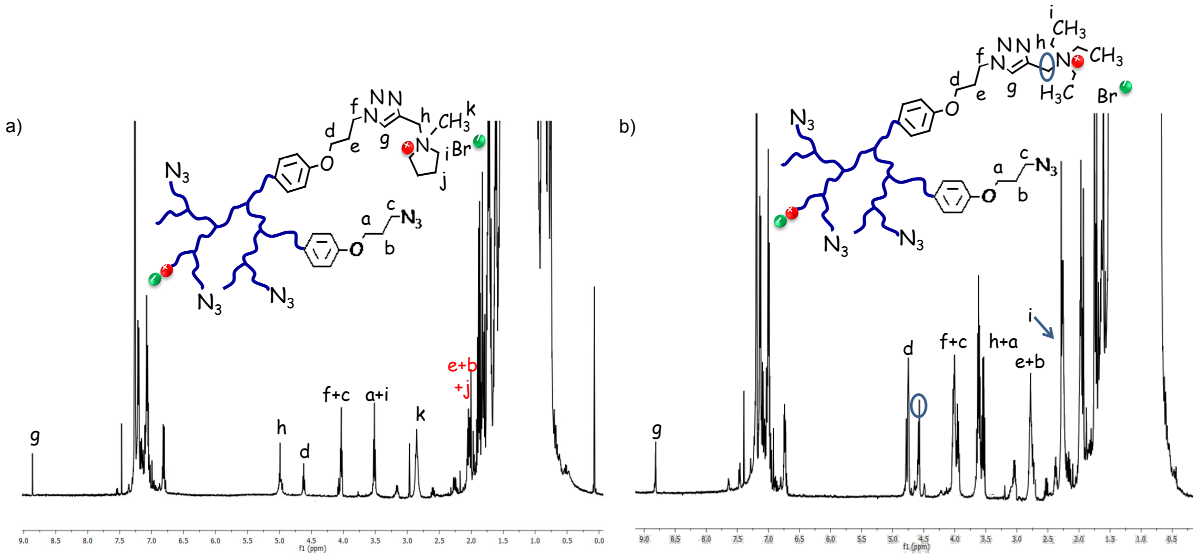


Electronic Supplementary Material (ESI) for Polymer Chemistry

S2 ^{1}H-NMR-spectrum of hyperbranched alkyne-functionalized PIB (**2**) after 20 hours quenching with TMPPS (30 equ. of inimer). IM / IB = 0.006.



S3 ^{1}H-NMR-spectrum of hyperbranched PIBs containing an ionic moiety: a) **4a**, b) **4b**.



2. Kinetic investigations of inimer-type living carbocationic polymerization via inline FTIR-measurements.

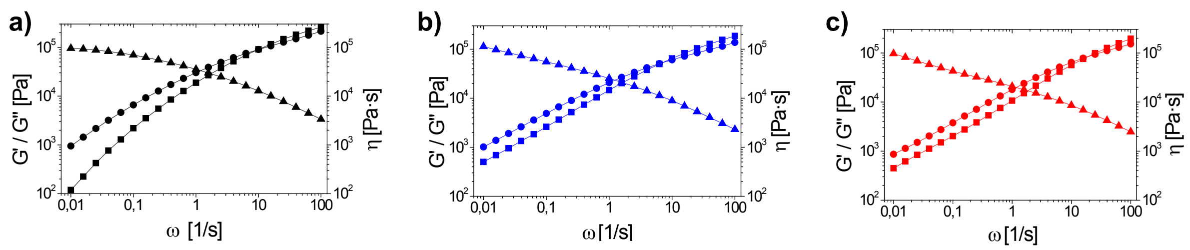
Table S1 Kinetic investigations of inimer-type living carbocationic polymerization via inline FTIR-measurements: determination of k_{app} out of first-order kinetic plots and calculation of the propagation constant k_p and the run number (*RN*).

Entry	inimer / IB	$[IB]_0$ ($mol \cdot L^{-1}$)	k_{app} (10^2 s^{-1})[a]	k_p (10^8 $s^{-1}M^{-1}$)[b]	*RN*[c]
1	0.010	2.30	2.03	1.27	3.88
2	0.006	1.91	0.92	2.65	6.73
3	0.004	2.00	0.34	3.37	8.98

[a]Determined by inline FTIR-spectroscopy $\ln[M]_0/[M]_t$ plot. [b]Determined by calculation k_{-i} =7.5·10^7 1/s, k_i=15 1/(s M^2)[1] with k_p determined by combination of following equations: $ln[M]_0/[M]_t = k_{app}t$ and $k_{app}=k_pK_{eq}I_0[LA]_0^2$ with respect to the dimeric form of the LA.[2] [c]Determined by calculation $RN=(k_p[P_n^+Ti_2Cl_9^-][M])/(k_{-i}[P_n^+Ti_2Cl_9^-])=k_p[M]/k_{-i}$.

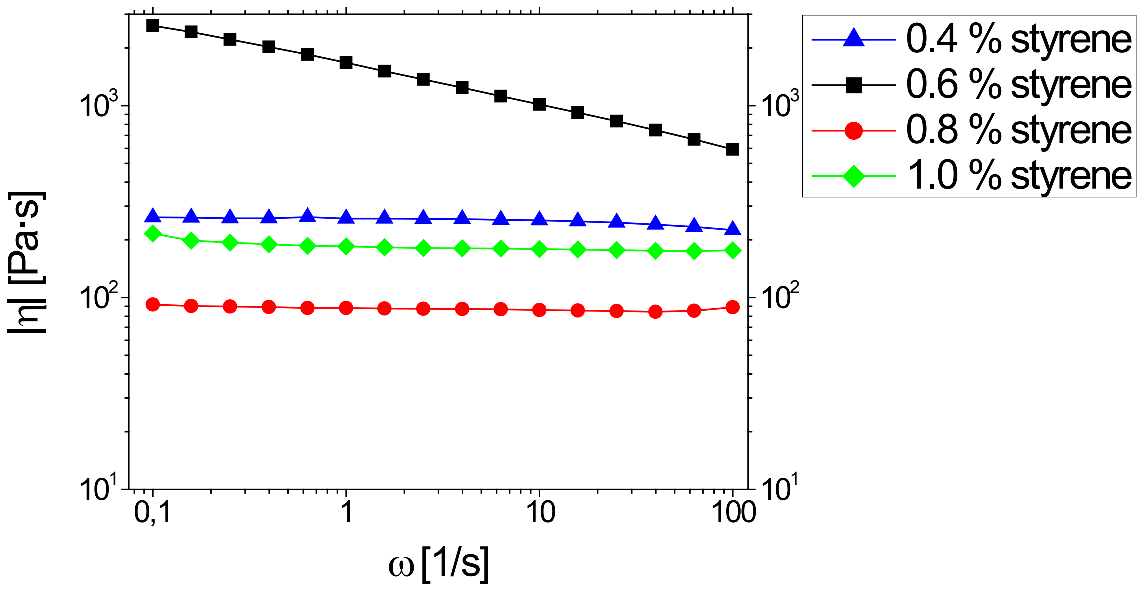
4. Rheology investigations of the pure hyperbranched polymers 4a-4b and 1b.

S4 Frequency sweep measurements of selected hyperbranched PIBs at 20°C a) **1b**, b) **4a** and c) **4b**



5. Rheology investigations of poly(isobutylene-*co*-styrene)s prepared via LCCP[3]:
0.4 % styrene (M_n = 13,200 g/mol, M_w/M_n= 1.34), 0.6 % styrene (M_n = 11,700 g/mol, M_w/M_n= 1.33), 0.8 % styrene (M_n = 10,900 g/mol, M_w/M_n= 1.30), 1.0 % styrene (M_n = 7,300 g/mol, M_w/M_n= 1.23).

S5 Absolute value of the viscosity versus frequency of containing —▲— 0.4 % styrene, —■— 0.6 % styrene, —●— 0.8 % styrene and —◆— 1.0 % styrene.



1. R. F. Storey and Q. A. Thomas, *Macromolecules*, 2003, **36**, 5065-5071.
2. J. E. Puskas, S. W. P. Chan, K. B. McAuley, S. Shaikh and G. Kaszas, *J. Polym. Sci. Part A: Polym. Chem.*, 2005, **43**, 5394-5413.
3. G. Kaszas, J. E. Puskas, J. P. Kennedy and W. G. Hager, *J. Polym. Sci. Part A: Polym. Chem.*, 1991, **27**, 427-435.