Supplementary material for :

Grafting poly(isobutylene) from nanoparticle surfaces: concentration and surface effects on livingness

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Determination of the amount of initiating-sites on the surface of **NP1**:

A) 1 g NP($AE200_{dry}$) was modified with CECE and used for subsequent polymerization immediately. ([I]~5 mM; [$TiCl_4$]=80 mM; [DMA]=5 mM; [DTBP]=3 mM; DCM:n-hexane=1:2, T=(–80 to -65 °C)) All yields are between 95 and 100%.

IB		**[IB]/[I]**	**$M_{n(th)}$**	**$M_{n(GPC)}$**	**$M_{n(th)}/M_{n(GPC)}$ %**
g	mol				
7.37	0.13	178	10 000	17 500.00	57.14
14.74	0.26	356	20 000	31 500.00	63.49
22.11	0.39	535	30 000	46 000.00	65.22
average					**61.95**

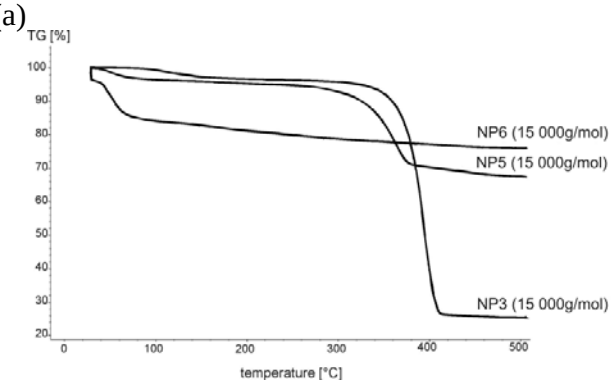
The $M_{n(th)}$ was calculated using the literature known value of 0.737 mmol Si-OH-goups /g of silica-NP (r=6 nm). Comparing the obtained M_n with the calculated one, the average number of polymers bound to the surface could be calculated. ($N_{(Ini)}$=0.737*0.6195=0.457 mmol/g NP; total surface of the NP's used: 200 m^2/g; using this one can calculate 0.85 initiator-molecules/nm^2)

B) <u>TGA-data:</u>

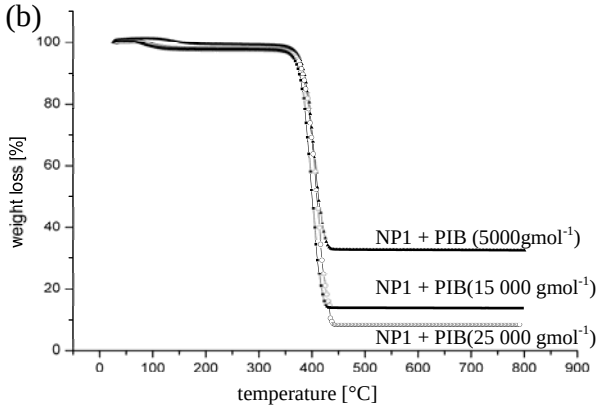
	% silica (th)	**% silica (TGA)**	**Error**
NP1 with 17 500 g/mol	11.9	12.8	+ 7.6 %
NP1 with 31 500 g/mol	6.4	6.8	+ 6.3 %
NP1 with 46 000 g/mol	4.3	4.1	- 4.7 %

These data clearly indicates that about 60-65% of the surface-binding sites (theoretical ~1.2 sites/nm^2) are modified with the initiator (CECE) resulting in an average binding-density of 0.85 molecules/nm^2.

(a)



(b)

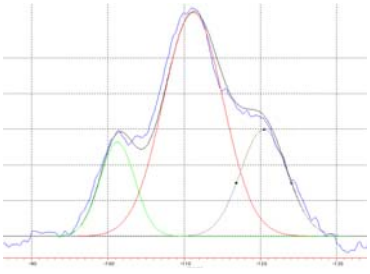


temperature [°C]

TGA's curves of NP's with different surface densities of initiator. (a) **NP6** (table 2) (15 000g mol^{-1}): found: 5% (calc.:6%); **NP5** (PIB 15 000g mol^{-1}): found: 20% (calc.:25%) and **NP3** (15 000g mol^{-1}): found: 70% (calc.:76%) (b) **NP1** with 5 000 g mol^{-1} PIB; **NP1** with 15 000 g mol^{-1} PIB, **NP1** with 25 000 g mol^{-1} PIB.

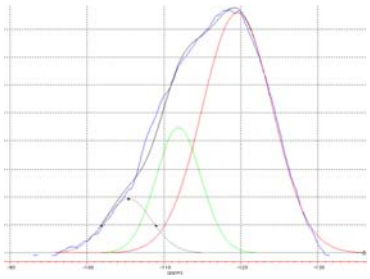
(C) **^{29}Si-solid state NMR (400 MHz, 4 mm rotors, rotation : 2000 Hz, CPMAS-mode, enabling to selectively monitor only the surface-bound ^{29}Si-nuclei).**

Aerosil 200



Q_2=0,89
Q_3=2,1
Q_4=1

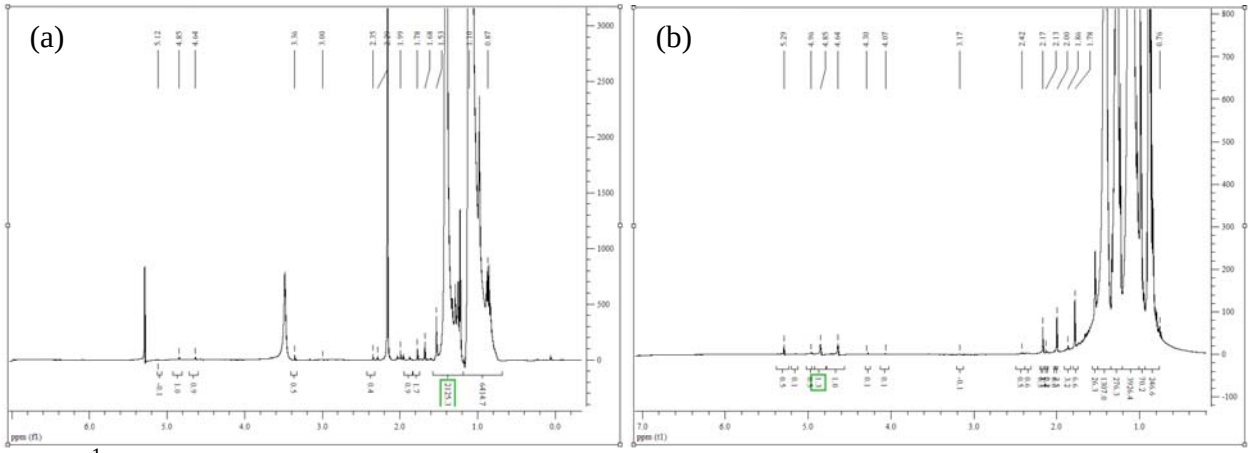
Aerosil 200+CECE



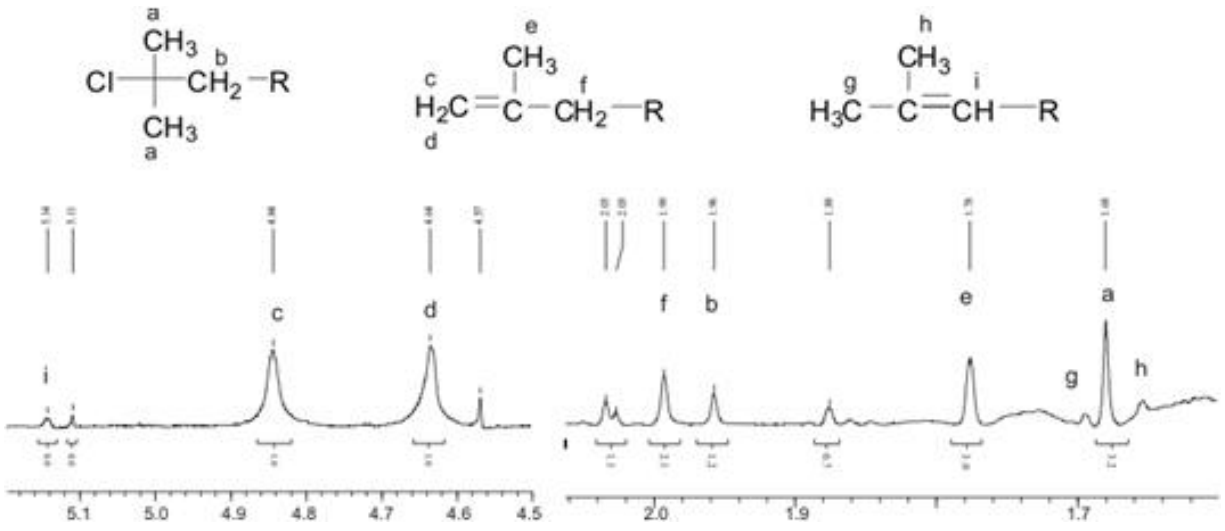
Q_2=0,07
Q_3=0,7
Q_4=1

The number of bound initiators and accordingly the completeness of the surface-reaction could be analyzed using ^{29}Si-CPMAS-NMR spectroscopy. ^{29}Si CPMAS NMR spectroscopy was measured on a Bruker Avance DRX 400 spectrometer with a 4mm probehead at a frequency of 79.4905 MHz. The samples were filled into 4 mm zirconia rotors which were spun at 4000 Hertz. The spectra were acquired in the cross 3 polarization mode using contact times of 10 ms and high power dipolar decoupling to reduce line broadening. The pulse repetition time was 5 s and between 10 000 and 30 000 scans were used to achieve sufficient signal to noise ratio.
The decreasing value of Q^2 (0.89$\rightarrow$ 0.07) and Q^3 (2.1 $\rightarrow$ 0.7) groups indicates that at least two-thirds of the surface groups of the NP's were modified during the modification. (60-65% of all groups modified)

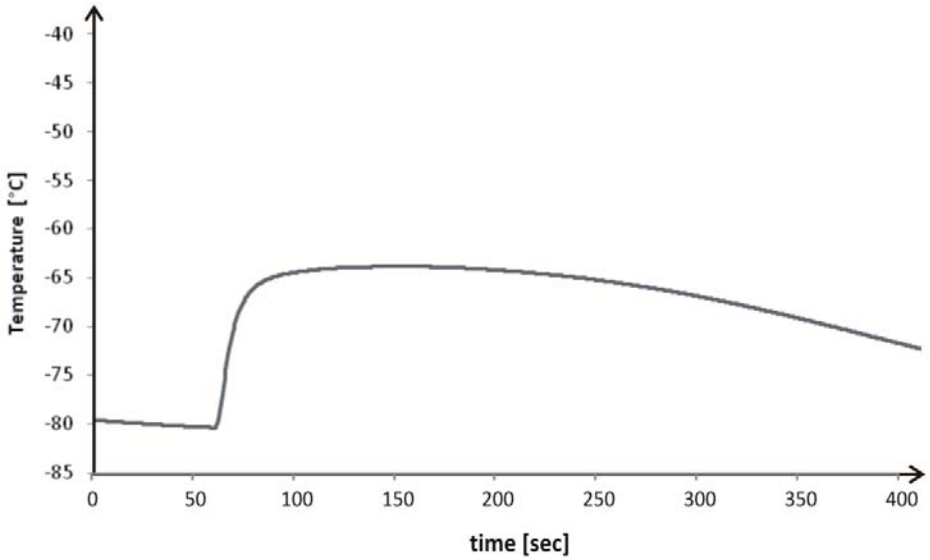
^{1}H- NMR-spectra of NP3 and PIB-grafted NP1 (400 MHz)



(a) ^{1}H-NMR-spectrum of **NP3** with 55 555 g/mol PIB and (b) of PIB-grafted **NP1** with 50 000g/mol PIB (0,8 chains/nm^{2})



^{1}H-NMR-spectra of endgroup-analysis of **NP1**, **NP2** and **NP3** (a) ppm-region from 4.5 – 5.2 ppm (b) ppm-region from 1.6 – 2.1 ppm.



Temperature-profile during a standard grafting-from polymerization (**NP1**), monitored via inline- IR-spectroscopy.