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## **Synthesis with Single Macromolecules: Covalent Connection between a Neutral Dendronized Polymer and Polyelectrolyte Chains as well as Graphene Edges**

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The wavelength of the UV light (254 nm) used for the *in-situ* cross-linking experiment has to overlap with the absorption of the peripheral azide groups of the polymer **PG3A** in order to induced the photolysis of the azide-groups to highly reactive nitrenes used in the cross-linking experiment. For clarity UV-vis spectra of **PG3A** and a chemically similar, but not azide functionalized polymer **PG3** were taken in solution (chloroform,  $c = 0.01$  mg/ml) using a Shimadzu UVP-2101-PC UV-vis spectrometer (resolution of 1 nm, quartz-cell, thickness 0.5 mm). Figure S-1a shows the UV-vis spectra of **PG3A** and **PG3**. Differences in the spectra of the two polymers arise from the peripheral azide-groups of the **PG3A**. In comparison to the spectra the typical phenyl-azide

absorption shows, a peak is observed at a wavelength of 471 nm (2) and a shoulder around 270 nm (1), besides the absorption of the aromatic core of **PG3A** around 240 nm. The photolysis of azide carrying **PG3A** was monitored during sequential illumination with a wavelength of 254 nm using the spectrometer's monochromator as shown in Fig. S-1b. The shoulder around 270 (1) and the peak (2) at 471 nm vanish on a time scale of 740 s of UV illumination, which shows that the wavelength of 254 nm used for UV illumination in the cross-linking experiment overlaps sufficiently with the azide absorption band around 270 nm to cause a covalent cross-linking.

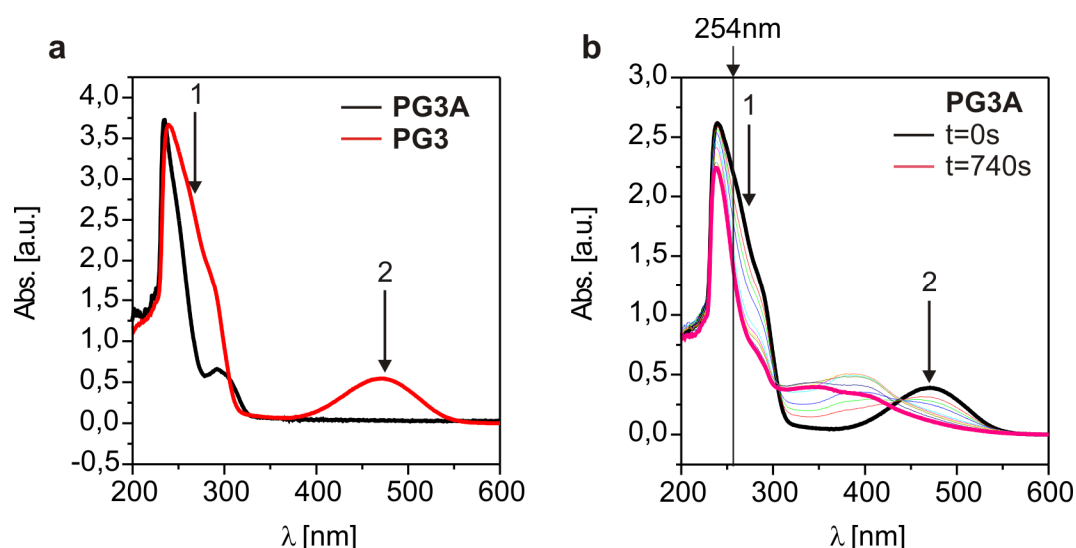


Fig S-1: (a) UV-vis spectra of the azide functionalized Polymer **PG3A** and a non functionalized but chemically similar dedronized polymer **PG3**. (b) The photolysis of the peripheral azide of **PG3A** caused by a UV illumination at a wavelength of 254 nm.

Since in UV-vis spectroscopy the specific azide absorption of the azid carrying **PG3A** overlaps with the absorption of the polymer core the illumination time needed for a successful cross-linking experiment was determined in model experiments monitoring the kinetics of the photolysis of the azide by Fourier-transform absorption infrared spectroscopy (FTIR) since the asymmetric stretch band of the azide is not overlapping

with the vibration modes of the core polymer. For that purpose, thin films (about 120 nm) of **PG3A** were prepared on *p*-doped silicon (Siegert Consulting, thermally grown oxide layer of 50 nm) cut into 10x10 mm<sup>2</sup> pieces by spin-coating 30 $\mu$ l of a solution of **PG3A** in chloroform (1.2 mg/ml) onto the silicon substrate rotating with 10 rps, followed by drying for 24 h under ambient conditions. The thickness of the so prepared films was determined by scratching the film with a sharp needle followed by measuring the step height of the so induced scratches by SFM. FTIR-spectroscopy measurements were performed with a Bruker IFS-66v spectrometer (resolution of 2.8cm<sup>-1</sup>, near-normal transmission geometry) using a midrange mercury cadmium telluride detector cooled with liquid nitrogen. For monitoring the decay of peripheral azide-groups of the **PG3A** during UV-illumination the standard spectral Ne-Hg lamp with a maximum emission at a wavelength of 254 nm (Pen-Ray 11SC-1, UVP Inc. Upland, CA, USA) was directly placed in the sample chamber of the FTIR-spectrometer. Figure S-2a displays the geometry of the setup inside of the sample-chamber of the FTIR-spectrometer with the UV-lamp placed relative to the sample in the same geometry as used in the SFM experiments. The characteristic asymmetric stretch band of the azide (double peak at  $\nu_1 = 2103 \text{ cm}^{-1}$ ,  $\nu_2 = 2119 \text{ cm}^{-1}$ ) can be clearly observed in the absorption spectra shown in Figure S-2b. While illuminating the sample sequentially with UV-light at 254 nm this band decays with time. Figure S-2c displays the normalized absorption at  $\nu = 2119 \text{ cm}^{-1}$  vs. illumination time, which may be fit to a bi-exponential decay with a fast,  $\tau_1 = 50 \pm 0.7 \text{ s}$ , and a slow component  $\tau_2 = 1096 \pm 17 \text{ s}$  (Figure S-2d). The two time constants may be assigned to azides near the surface and in the bulk of the film, respectively. The slow component can be explained by the absorption of a portion of the UV light in the bulk caused by the aromatic moieties of the polymer core. In the later cross-linking experiments, where the peripheral azide-groups of individual strands of the **PG3A** have to be photolyzed to give the required

highly reactive nitrenes, the sample therefore had to be illuminated for approximately 161 s in order to photolyze 63 % (1/e) of the polymer's azides. Since also the pyramidal SFM-tip can shadow the area of interest, the tip was moved outside of the monitored scan-area during UV-illumination and the time was raised to 5 min to guarantee an effective cross-linking.

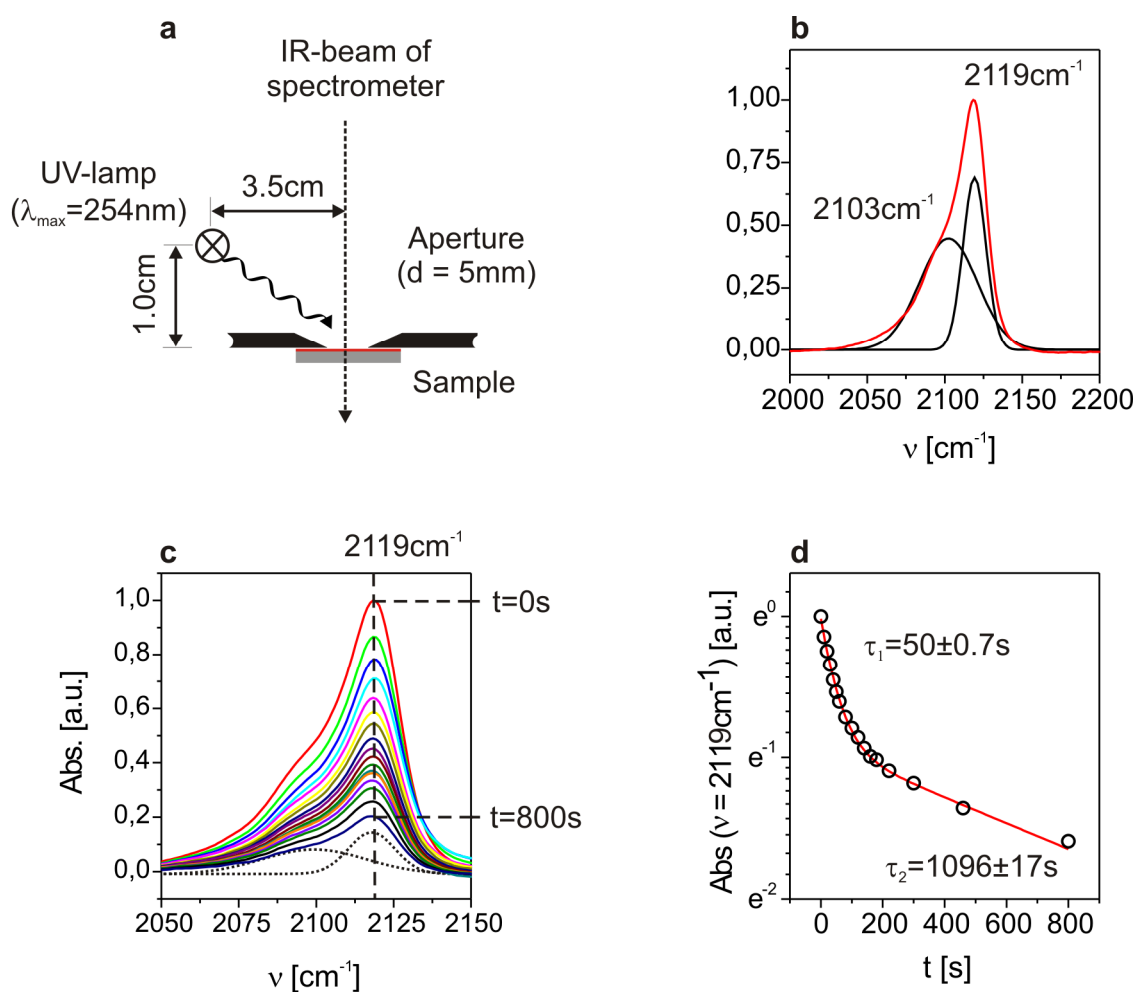


Figure S-2: (a) Setup for FTIR-spectroscopy on a film of **PG3A** on silicon in the geometry used in the SFM cross-linking experiment. (b) Characteristic asymmetric stretch band of the azide-groups ( $\nu_1 = 2103 \text{ cm}^{-1}$ ,  $\nu_2 = 2119 \text{ cm}^{-1}$ ). (c) Decay of the absorption at  $\nu = 2119 \text{ cm}^{-1}$  over time. (d) Fit of decay function to two exponentials with  $\tau_1 = 50 \pm 0.7 \text{ s}$  and  $\tau_2 = 1096 \pm 17 \text{ s}$ .