

Electronic Supplementary Information (ESI)

Shielding effects in spacious macromolecules: a case study with dendronized polymers

Chiara Gstrein,^a Peter Walde,^a A. Dieter Schlüter^a and Thomas Nausner^{*b}

^a Laboratory of Polymer Chemistry, Department of Materials, ETH Zürich, Vladimir-Prelog Weg 5, CH-8093 Zürich, Switzerland.

^b Laboratory of Inorganic Chemistry, Department of Chemistry and Applied Biosciences, Vladimir-Prelog Weg 2, ETH Zürich, CH-8093 Zürich, Switzerland.

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1. Materials and methods

The labelled denpols *l*-**PG1** to *l*-**PG4** were the same as the ones in a previous work, see **Table S1**.^[S1]

The unlabelled denpol **PG3** was synthesized by Daniel Messmer by using the procedure described before.^[S2]

N-MNA (*N*-methyl-4-nitroaniline) was from Aldrich Chemicals, 2-propanol (isopropanol, puriss. p.a. 99.8%) and acetone (Chromasolv 99.9%) were from Sigma-Aldrich and used as received.

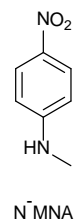


Table S1

Number and weight average molar masses (M_n and M_w), number average degree of polymerization (P_n = average number of repeating units (r.u.) per denpol chain), and polydispersity index (PDI = M_w/M_n) of the denpols used.^[S1]

Denpol ^a	$M_n / \text{g}\cdot\text{mol}^{-1}$	$M_w / \text{g}\cdot\text{mol}^{-1}$	$P_n / -$	PDI / -
<i>l</i> - PG1	281 000	1 090 000	538	3.9
<i>l</i> - PG2	926 000	2 420 000	761	2.6
<i>l</i> - PG3	2 350 000	5 970 000	902	2.5
<i>l</i> - PG4	2 480 000	15 300 000	461	6.2
PG3	1 742 000	3 106 000	664	1.8

^a Please note that in ref. [S1] the labelled denpols *l*-**PG1** to *l*-**PG4** are abbreviated as *ls*-**PG1** to *ls*-**PG4**

For the pulse radiolysis measurements of the labelled denpols *l*-**PG1** to *l*-**PG4** (raw data are shown in **Figure S2**), solutions were prepared by dissolving a defined amount of freeze-dried powders of the labelled denpols in a mixture of 2-propanol:acetone (95:5, v/v) at room temperature to yield a 4-nitroaniline concentration of 2 μM . Afterwards the solutions were degassed in a glove box over night before the pulse radiolysis measurements were carried out. For the control measurements, the solutions were prepared accordingly, whereas the concentration of repeating units in unlabelled **PG3** was the same as in the case of *l*-**PG3**. The degassing treatment was applied to all samples used for the control measurements, including the solvent mixture itself.

The pulse radiolysis measurements were carried out at the pulse radiolysis facility on the Höggerberg campus of the ETH Zürich.^[S3]

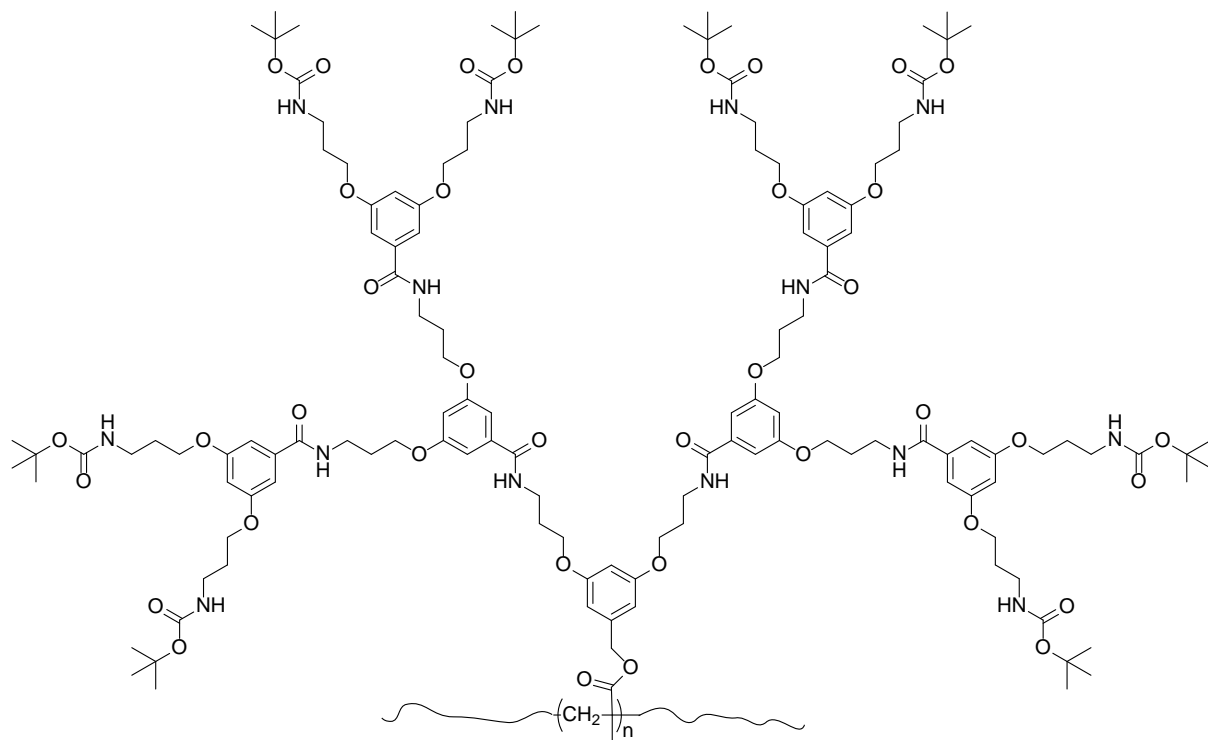
[S1] C. Gstrein, B. Zhang, M. Ahmed Abdel-Rahman, O. Bertran, C. Alemán, G. Wegner, A. D. Schlüter, *Chem. Sci.*, 2016, **XX**, XX-XX.

[S2] H. Yu, A. D. Schlüter, B. Zhang, *Macromolecules*, 2012, **45**, 8555-8560.

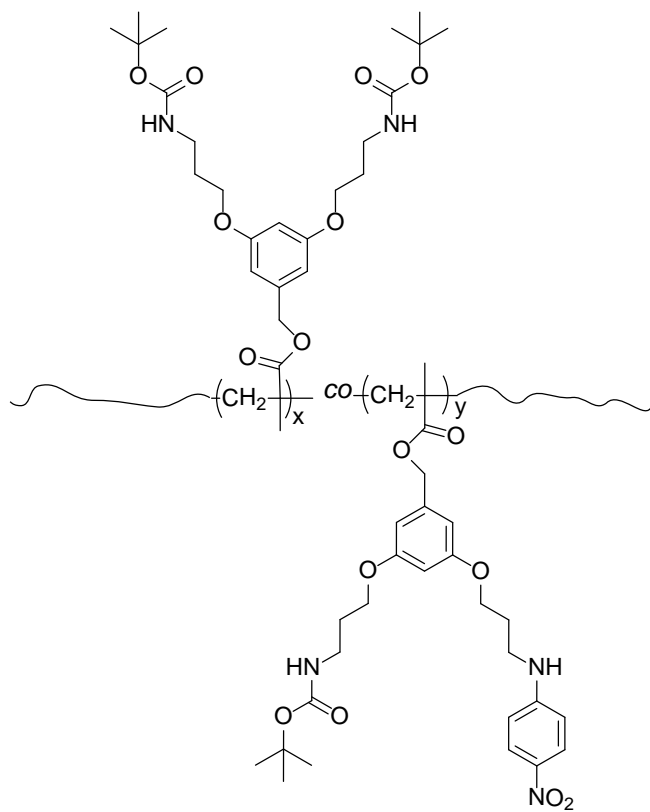
[S3] T. Nauser, G. Casi, W. H. Koppenol and C. Schöneich, *J. Phys. Chem. B*, 2008, **112**, 15034-15044.

Chemical structures of all denpols used

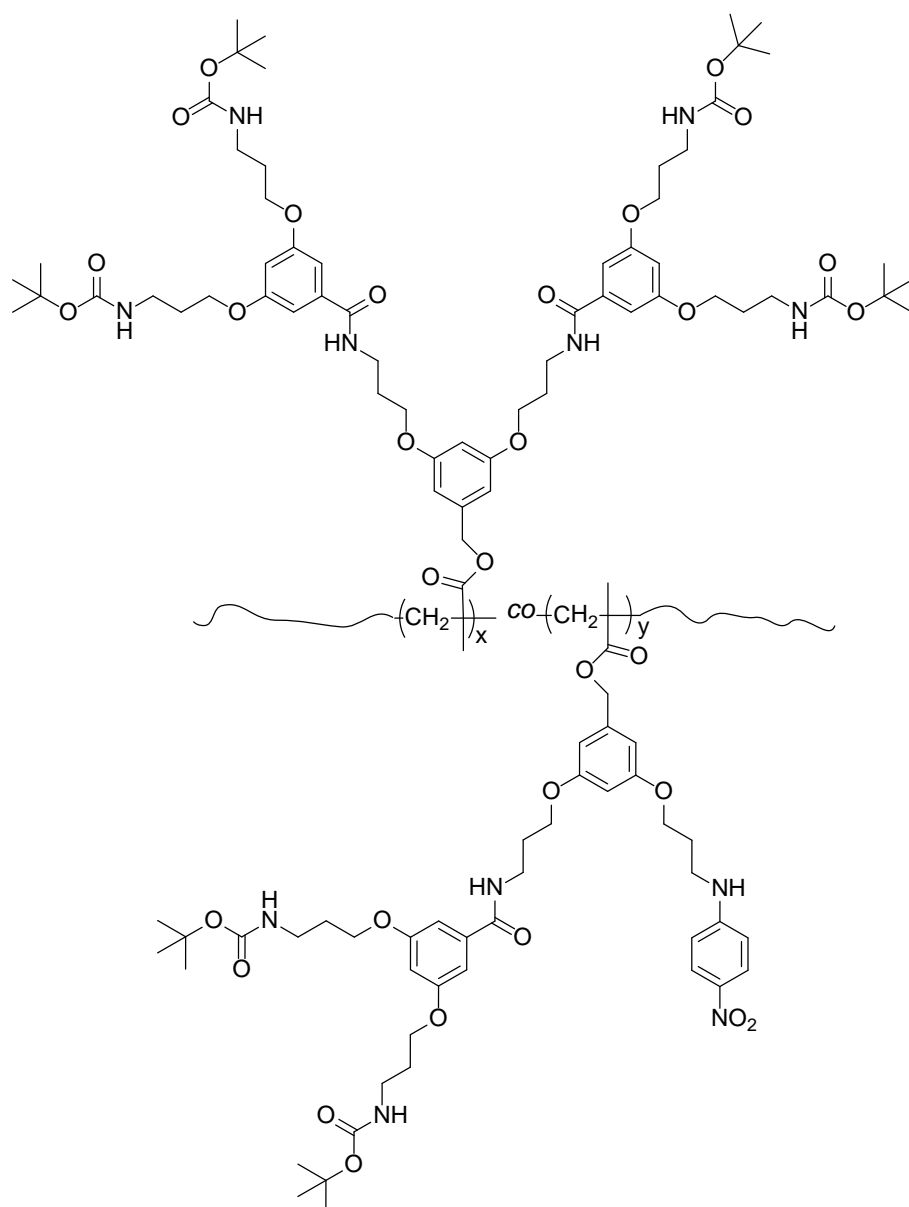
Denpol PG3



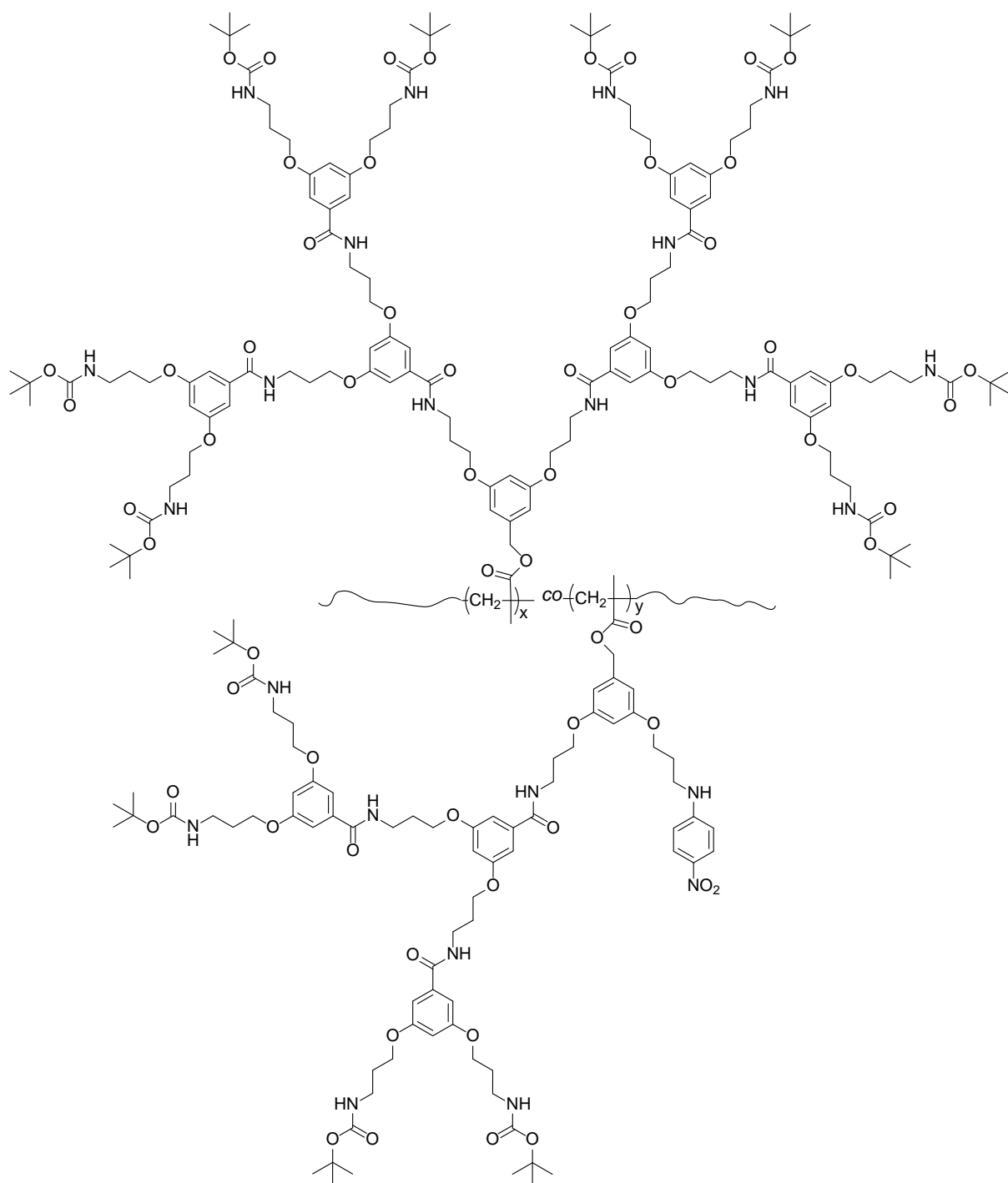
Denpol /-PG1



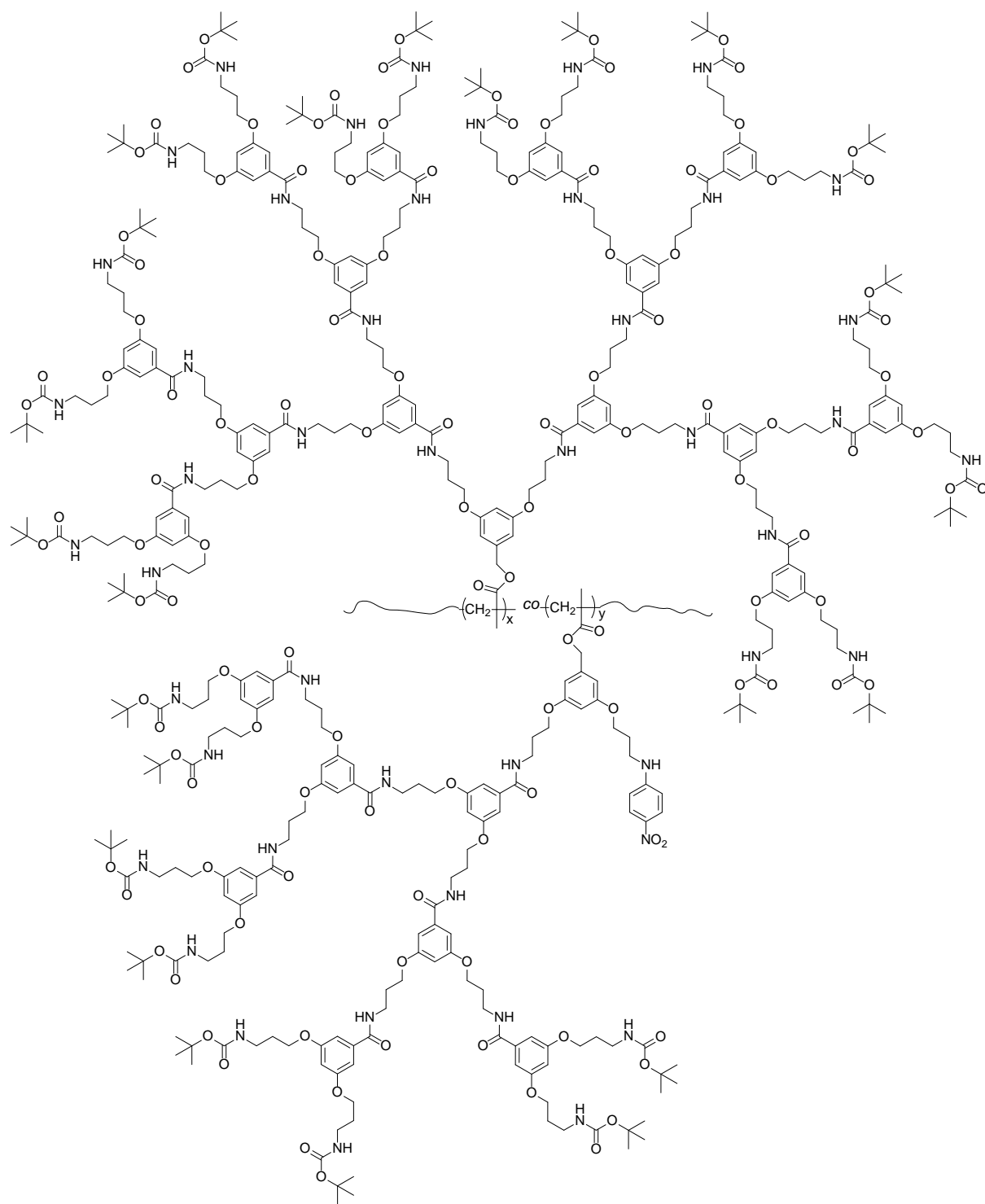
Denpol /-PG2



Denpol /-PG3



Denpol /-PG4



2. Control measurements by using the solvent mixture only

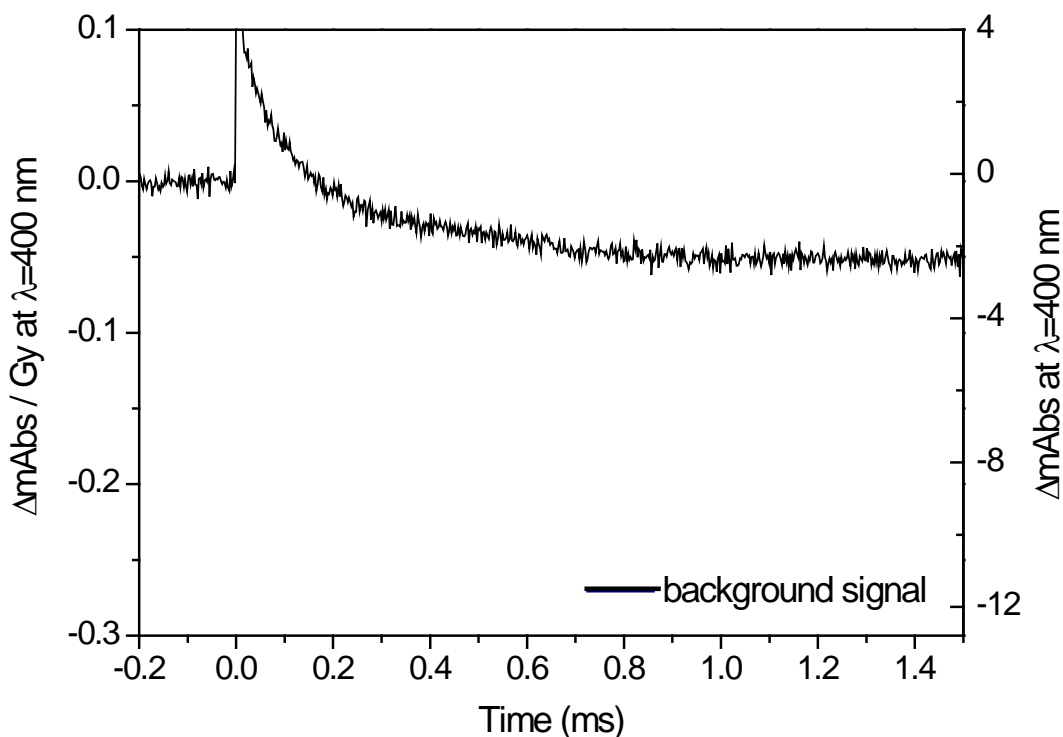


Figure S1

Control measurements by using the solvent mixture only (2-propanol:acetone, 95:5, v/v). The changes in absorbance at $\lambda = 400$ nm ($\Delta mAbs$) for this background reaction were recorded for the same dose as used in the measurements with the dendronized polymers (40 Gy). The traces are shown for the first 1.5 ms after irradiation of the solvent. This average was then subtracted from the measured traces for all labelled denpol samples (**Figure S2**) to obtain the data shown in **Figure 2**, *i.e.* the graphs shown in **Figure 2** are the measured traces (**Figure S2**) minus the averaged background trace (this figure). Please note that very small absolute signals (+0.004 – -0.012 ΔAbs) were recorded with a 6 cm measurement cell and an elevated dose of 40 Gy. These changes would not be detectable with instruments with a standard optical pathlength of 1 cm or with a more usual dose of < 5 Gy.

Ionizing radiation deposits energy in the solvent, which also causes heating and quick pressure changes (shock waves) in the solvent. Both alter the refractive properties of the sample. Similar effects are well known in stopped-flow and temperature-jump experiments with organic solvents. The heat capacity and the compressibility of the samples are governed by the solvent (> 95% w/w) and therefore, the optical effects on the sample by heating/pressure may be corrected by such controls.

3. Raw data for the measurements of the denpols

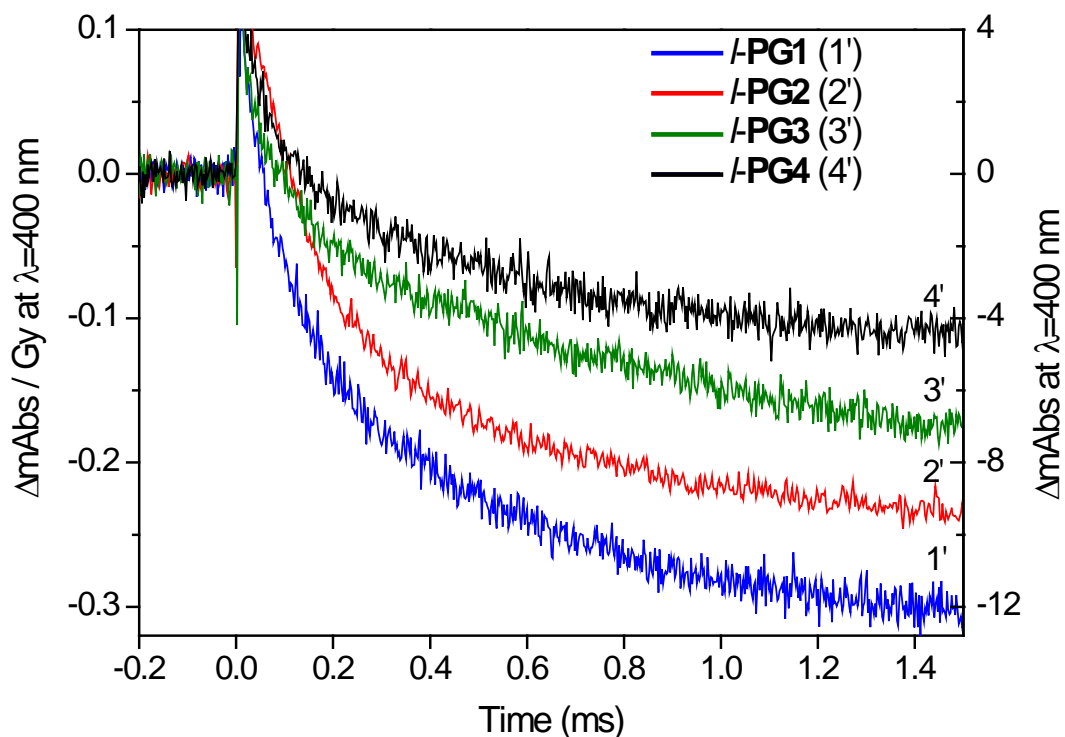


Figure S2

Raw data for the measurements of the dendronized polymers. Changes in the absorbance at $\lambda = 400$ nm ($\Delta mAbs$: difference in 10^{-3} absorbance units, $l = 6$ cm) upon pulsed irradiation (dose: 40 Gy) of solutions of the 4-nitroaniline-labelled dendronized polymers *l*-PG1 (1'), *l*-PG2 (2'), *l*-PG3 (3'), and *l*-PG4 (4'), see **Chemical structures** above. Absorbance changes are shown for the first 1.5 ms after irradiation (at $t = 0$) at room temperature ($T \approx 25$ °C). Solvent: 2-propanol:acetone, 95:5 (v/v). Concentrations of the dendronized polymers: 0.1 mM r. u. (2 % carrying a 4-nitroaniline unit).