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A Dimethacrylate Cross-linker Cleavable Under Alkaline Hydrolysis Conditions or Thermally: Synthesis, Polymerization, Degradation

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Experimental

Materials. 2,6-Lutidine (96%), paraformaldehyde (reagent grade, crystalline), methacryloyl chloride (97%), methyl methacrylate (MMA, 99%), 2-cyanoprop-2-yl dithiobenzoate (2-CPDB, 97%), 1,4-dioxane (99.8%), 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH, 95%), calcium hydride (CaH_2, 90-95%), sodium carbonate (≥99.5%), potassium carbonate (≥99%), basic alumina (60 Å, 150 mesh, pH = 9.5 ± 0.5), *n*-hexane (≥97%) and sodium deuteroxide (40 wt.% in D_2O, 99.5 atom % D) were purchased from Aldrich, Germany. Synthesis grade triethylamine (≥99%) and tetrahydrofuran (THF, 99.8%) were obtained from Scharlau, Spain. HPLC grade THF was also purchased from Scharlau and was used as the mobile phase in gel permeation chromatography. 2,2′-Azobis(isobutyronitrile) (AIBN, 95%), silica gel (60-400 mesh), sodium hydroxide (99%), dimethyl sulfoxide (DMSO, 99%), deuterated dimethyl sulfoxide (d_6-DMSO, 99.9%), and deuterated chloroform ($CDCl_3$, 99.8%) were purchased from Merck, Germany. Finally, acetone (99.5%) was from Lab Scan, Ireland.

Synthesis of 2,6-Pyridinediethanol. 2,6-Pyridinediethanol was prepared from the reaction of 2,6-lutidine with paraformaldehyde in water under conditions of elevated pressure and temperature [1,2]. In particular, 2,6-lutidine (50 mL, 46.26 g, 0.4317 mol), paraformaldehyde (25.92 g, 0.8634 mol of formaldehyde units) and H_2O (25 mL) were transferred to a 500-mL round-bottomed pressure flask with an Ace-Thread 15 PTFE front-seal plug, containing a magnetic stirring bar. The mixture was stirred and heated at 135 °C for 12 h. Subsequently, the reaction mixture was cooled down to room temperature, and a few drops of sodium carbonate solution were then added to it. The unreacted 2,6-lutidine was removed by steam distillation, and the residue

was evaporated on a steam bath until the distillation stopped at 100 °C. Afterwards, potassium carbonate was added and the resulting (mixture of) organic bases was extracted with chloroform (3 × 200 mL). Then, the solvent was removed, and the by-product, 2-(6-methylpyridin-2-yl)ethanol, was distilled off on the vacuum line at 80 °C. The residue was a mixture of two isomeric diols, 2,6-pyridinediethanol and the side product 2-(6-methylpyridin-2-yl)propane-1,3-diol. The mixture was separated by column chromatography (*n*-hexane/acetone) in a solvent mixture of varying composition, starting with a 90/10 *n*-hexane/acetone mixture. Pure 2-(6-methylpyridin-2-yl)propane-1,3-diol eluted at a 65/35 *n*-hexane/acetone solvent composition (5 g, 6.5%), while pure 2,6-pyridinediethanol (1.2 g, 1.6%) eluted at a 35/65 *n*-hexane/acetone composition. The diols were characterized using ^{1}H and ^{13}C NMR spectroscopy, and differential scanning calorimetry. **^{1}H NMR 2,6-pyridinediethanol ($CDCl_3$, δ):** 2.90 ppm (t, -CH_2-C*H*$_2$OH, 4 H), 3.90 ppm (t, -C*H*$_2$$CH_2$OH, 4 H), 4.50 ppm (s, -$CH_2$-$CH_2$O*H*, 2 H), 6.95 ppm (d, aromatic, 2H), 7.45 ppm (d, aromatic, 1 H). **^{13}C NMR ($CDCl_3$, δ):** 39.56 ppm (s, -*C*H_2-CH_2OH, 2 C), 61.39 ppm (s, -CH_2*C*H_2-OH, 2 C), 121.06 ppm (s, aromatic, 2 C), 136.94 ppm (s, aromatic, 1 C), 158.86 ppm (s, aromatic, 2 C). **^{1}H NMR (2-(6-methylpyridin-2-yl)propane-1,3-diol) ($CDCl_3$, δ):** 2.43 ppm (s, -C*H*$_3$, 3 H), 2.95 ppm (q, -C*H*-(CH_2OH)$_2$, 1 H), 3.95 – 4.00 ppm (m, -CH-C*H*$_2$OH, 4 H), 4.70 ppm (s, -CH-CH_2O*H*, 2 H), 6.98 ppm (m, aromatic, 2 H), 7.47 ppm (t, aromatic, 1 H). **^{13}C NMR ($CDCl_3$, δ):** 23.83 ppm (s, -*C*H_3, 1 C), 48.70 ppm (s, -*C*H-CH_2-OH, 1 C), 62.88 ppm (s, -CH-*C*H_2OH, 2 C), 119.96 ppm (s, aromatic, 1 C), 121.14 ppm (s, aromatic, 1 C), 136.70 ppm (s, aromatic, 1 C), 156.95 ppm (s, aromatic, 1 C), 160.61 ppm (s, aromatic, 1 C).

Synthesis of 2,6-Pyridinediethanol Dimethacrylate (PyDMA). The PyDMA cross-linker was prepared by the esterification of 2,6-pyridinediethanol with 40% molar excess of methacryloyl chloride. In particular, 2,6-pyridinediethanol (2.4 g, 0.0144 mol; two purified batches), Et_3N (32 mL, 23.24 g, 0.2296 mol) and absolute THF (15 mL) were transferred to a 100-mL round-bottomed flask containing a magnetic stirring bar. The solution was stirred and cooled down to 0 °C. After stabilization of the temperature, methacryloyl chloride (3.93 mL, 4.2 g, 0.0402 mol) was added dropwise using a glass syringe and the reaction was stirred for 2 h at 0 °C. Subsequently, the mixture was filtered and passed twice through a basic alumina column to remove methacrylic acid (hydrolysis product of excess methacryloyl

chloride) and any other acidic impurities. Then, the solvent was evaporated off to give pure cross-linker in 60% yield. Afterwards, PyDMA was stirred for at least 24 h over CaH_2 to remove all the moisture and the last traces of protonic impurities, and was, finally, filtered just prior to the polymerizations. The thus-purified PyDMA was characterized using ^{1}H and ^{13}C NMR spectroscopy. **^{1}H NMR (d_6-DMSO, δ):** 1.88 ppm (s, CH_2=CCH_3, 6 H), 3.12 ppm (t, -CH_2CH_2O, 4 H), 4.50 ppm (t, -CH_2CH_2O, 4 H), 5.51 ppm (s, CH_2=CCH_3 H *trans* to CO_2, 2 H), 6.03 ppm (s, CH_2=CCH_3 H *cis* to CO_2, 2 H), 7.04 ppm (d, aromatic, 2 H), 7.53 ppm (t, aromatic, 1 H). **^{13}C NMR (d_6-DMSO, δ):** 17.77 ppm (s, CH_2=CCH_3, 2 C), 36.41 ppm (s, -CH_2CH_2O, 2 C), 63.44 ppm (s, -CH_2CH_2O, 2 C), 121.10 ppm (s, aromatic, 2 C), 125.40 ppm (s, CH_2=CCH_3, 2 C), 135.78 ppm (s, CH_2=CCH_3, 2 C), 136.74 ppm (s, aromatic, 1 C), 157.32 ppm (s, aromatic, 2 C), 166.33 ppm (s, CO_2, 2 C).

Polymerizations

RAFT Polymerization. RAFT polymerization was used for the syntheses of the hyperbranched homopolymer and the polymer networks. The hyperbranched homopolymer (composed only of cross-linker) was prepared by the polymerization of the cross-linker at low concentration (0.66 M), whereas a higher cross-linker concentration (2.50 M) was employed for the preparation of the insoluble polymer gel. 2-CPDB was used as the chain transfer agent (CTA), AIBN served as the initiator, while 1,4-dioxane was employed as the solvent.

Synthesis of the $PyDMA_{10}$ Hyperbranched Homopolymer. AIBN (0.0067 g, 0.0412 mmol) and 2-CPDB (0.0145 g, 0.0659 mmol) were dissolved in 1,4-dioxane (0.8 mL), and the resulting solution was transferred to a 50-mL round-bottomed flask, fitted with a glass valve, containing PyDMA (0.2 g, 0.6593 mmol) and a magnetic stirring bar. The system was degassed by three freeze-pump-thaw cycles and it was, subsequently, placed in an oil bath thermostated at 65 °C for 24 h.

Synthesis of the $PyDMA_{10}$ Homopolymer Network. AIBN (0.0101 g, 0.0618 mmol) and 2-CPDB (0.0218 g, 0.0989 mmol) were dissolved in 1,4-dioxane (0.1 mL), and the resulting solution was transferred to a 50-mL round-bottomed flask, fitted with a glass valve, containing PyDMA (0.3 g, 0.9889 mmol) and a magnetic stirring bar. The system was degassed by three freeze-pump-thaw cycles and it was, subsequently, placed in an oil bath thermostated at 65 °C for 24 h.

Synthesis of the MMA_{100}-*co*-$PyDMA_8$ Polymer Network. AIBN (0.0126 g, 0.0771 mmol) and CPDB (0.0273 g, 0.1234 mmol) were dissolved in 1,4-dioxane (2.8 mL), and the resulting solution was transferred to a 50-mL round-bottomed flask, fitted with a glass valve, containing PyDMA (0.3 g, 0.9889 mmol), MMA (1.2355 g, 1.32 mL, 12.3404 mmol) and a magnetic stirring bar. The system was degassed by three freeze-pump-thaw cycles and it was, subsequently, placed in an oil bath thermostated at 65 °C for 24 h.

Alkaline Hydrolysis of the PyDMA Units. The PyDMA units in the PyDMA hyperbranched homopolymer were hydrolyzed in d_6-DMSO in the presence of sodium deuteroxide at room temperature. To this end, 0.1 g of the dried hyperbranched homopolymer was dissolved in 1.0 mL d_6-DMSO, and, to the resulting solution, 40 μL NaOD 40% in D_2O was added. The conversion of the PyDMA units to MAA units and 2,6-divinylpyridine was kinetically followed using ^{1}H NMR spectroscopy for 24 h. The alkaline hydrolysis of the PyDMA units in the $PyDMA_{10}$ homopolymer network and the MMA_{100}-*co*-$PyDMA_8$ copolymer network was performed by transferring 0.1 g of dried network in 1.0 mL d_6-DMSO containing 40 μL NaOD 40% in D_2O (final NaOD concentration of 0.4 M). The conversion of the PyDMA units to MAA units and 2,6-divinylpyridine was determined by analyzing the supernatant using ^{1}H NMR spectroscopy. In the case of the $PyDMA_{10}$ homopolymer network, alkaline hydrolysis of the PyDMA units led to the formation of MAA homopolymer, while in the case of the MMA_{100}-*co*-$PyDMA_8$ copolymer network, alkaline hydrolysis of the PyDMA units led to the formation of a MMA_{100}-*co*-MAA_{16} statistical copolymer.

Attempted Acidic Hydrolysis of the PyDMA Units. The PyDMA units in the PyDMA hyperbranched homopolymer were also subjected to acidic hydrolysis conditions in d_6-DMSO in the presence of deuterium chloride (final DCl concentration 0.4 M) at room temperature. ^{1}H NMR spectra were recorded for 24 h.

Thermolysis of the PyDMA Units. The hyperbranched polymer and the (co)polymer networks were thermolyzed at 130 °C in d_6-DMSO for 12 h. To this end, a small amount of the hyperbranched homopolymer or of each network was transferred to a 50-mL round-bottomed flask containing a magnetic stirring bar and 1.0 mL d_6-DMSO. The temperature was raised to 130 °C and the mixture was left to

react overnight. The conversion of the PyDMA units to MAA units and 2,6-divinylpyridine was analyzed using ^{1}H NMR spectroscopy.

Polymer Characterization

Gel Permeation Chromatography. The molecular weight distributions (MWDs) of all the soluble polymers (the hyperbranched polymer, the extractables from the polymer networks, and the cleavage products of MMA_{100}-*co*-$PyDMA_8$) were recorded using gel permeation chromatography (GPC). These MWDs were used to calculate the number-average molecular weights, M_n, the peak molecular weights, M_p, and the molecular weight dispersities ($Đ = M_w/M_n$; M_w is the weight-average molecular weight). For the GPC analyses, a Polymer Laboratories chromatograph was employed, together with a Polymer Laboratories ERC-7515A refractive index (RI) detector, and a single Polymer Laboratories PL-Mixed "D" column (bead size = 5 μm; pore sizes = 100, 500, 10^3 and 10^4 Å). The mobile phase was THF, delivered using a Waters 515 isocratic pump at a flow rate of 1 mL min^{-1}. All samples were filtered through 0.45 μm PTFE syringe filters just before analysis. The molecular weight calibration curve was based on ten narrow molecular weight (800, 2220, 6370, 12600, 23500, 41400, 89300, 201000, 392000 and 675000 g mol^{-1}) linear poly(MMA) standards supplied by Polymer Standards Service GmbH, Mainz, Germany.

NMR Spectroscopy. A 500 MHz Avance Bruker NMR spectrometer, equipped with an Ultrashield magnet, was used to acquire the ^{1}H and ^{13}C NMR spectra of all the synthesized low molecular weight compounds (alcohols, side-products and cross-linker) in $CDCl_3$ and the ^{1}H NMR spectra of all the soluble polymers (hyperbranched polymer, extractables from the polymer networkrs and all polymer cleavage products) in $CDCl_3$ or in d_6-DMSO.

DSC and TGA. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were performed using a Thermal Analysis Instruments (TA) differential scanning calorimeter model Q1000 and TA thermogravimetric analyzer model Q500, respectively. The temperature range for the DSC measurements was from 40 to 375 °C, whereas that for TGA was from 40 to 600 °C.

Determination of the Sol Fraction (Extractables). After their syntheses, the $PyDMA_{10}$ homopolymer network and the MMA_{100}-*co*-$PyDMA_8$ copolymer network

were characterized in terms of their sol fraction (extractables). To this end, each polymer network was transferred into a glass-jar containing THF, and allowed to equilibrate for 2 days in order to release its extractables. Subsequently, the THF solution of the extractables was transferred into a pre-weighed round-bottomed flask, where most of the THF was removed using a rotary evaporator. Further drying was accomplished in a vacuum oven for 24 h at room temperature. The remaining dried mass in the pre-weighed round-bottomed flask was measured, and the sol fraction was calculated as the ratio of the dried mass divided by the theoretical mass of the network (estimated as the sum of the masses of the monomer, the PyDMA cross-linker and the CTA). The extractables were finally analyzed using GPC and ^{1}H NMR spectroscopy to determine their molecular weight characteristics and their composition, respectively.

Measurement of the Degree of Swelling (DS) in THF. After the extraction of the sol fraction, the $PyDMA_{10}$ homopolymer network and the MMA_{100}-*co*-$PyDMA_{8}$ copolymer network were characterized also in terms of their degrees of swelling (DS) in THF. Three pieces from each THF-equilibrated network were placed in pre-weighed vials, and the THF-swollen mass of each piece was determined. Then, the vials containing the THF-swollen polymer pieces were dried in a vacuum oven at room temperature for 48 h. Subsequently, the dried pieces were re-weighed to determine their dry mass. Finally, the DSs in THF were calculated as the ratio of the swollen network mass divided by the dry network mass.

Results and Discussion – Further Figures

The most crucial reaction performed in this investigation was the one for the synthesis of 2,6-pyridinediethanol, which also resulted in the formation of two side-products, an isomeric diol, 2-(6-methylpyridin-2-yl)propane-1,3-diol, and a simple alcohol, 2-(6-methylpyridin-2-yl)ethanol. This reaction involves the hydroxymethylation of 2,6-lutidine (2,6-dimethylpyridine) using paraformaldehyde, and is illustrated in Figure S1 on the following page, together with the relevant products:

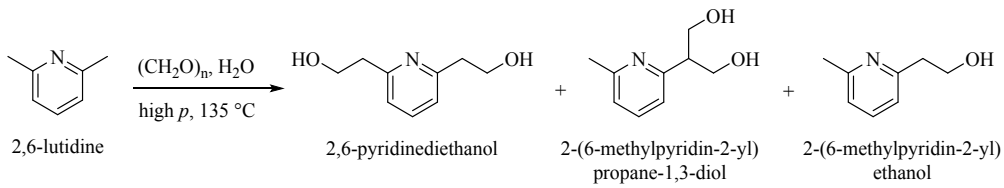

Figure S1. Hydroxymethylation of 2,6-lutidine and the resulting products.

Figure S2 presents (a) the ^{1}H and (b) the ^{13}C NMR spectra of purified 2,6-pyridinediethanol in $CDCl_3$.

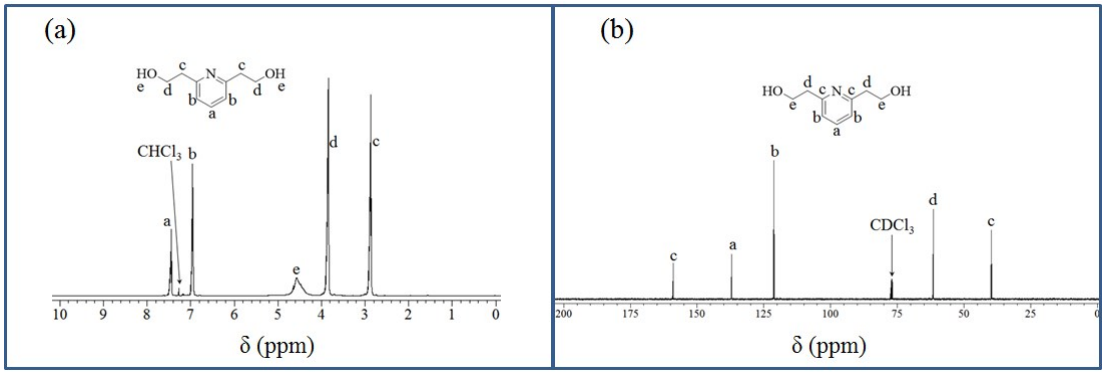

Figure S2. (a) ^{1}H and (b) ^{13}C NMR spectra of 2,6-pyridinediethanol in $CDCl_3$.

Figure S3 displays (a) the ^{1}H and (b) the ^{13}C NMR spectra of purified 2-(6-methylpyridin-2-yl)propane-1,3-diol in $CDCl_3$.

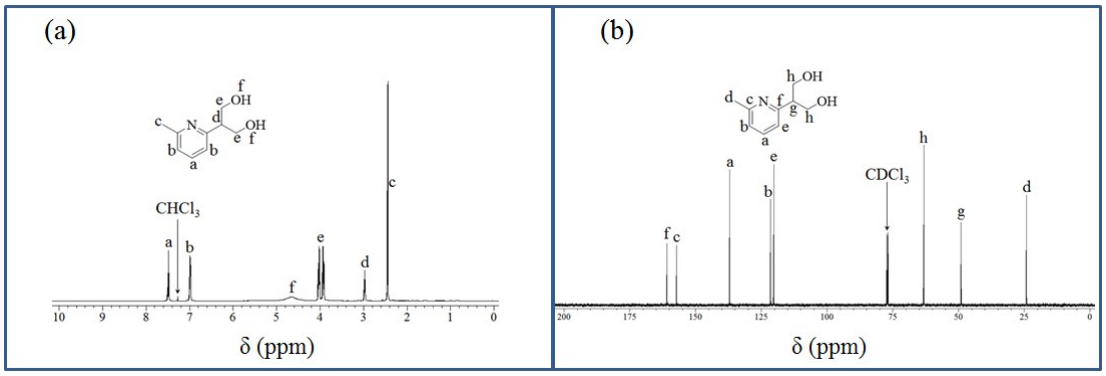

Figure S3. (a) ^{1}H and (b) ^{13}C NMR spectra of 2-(6-methylpyridin-2-l)propane-1,3-diol in $CDCl_3$.

Figure S4 shows the ^{1}H and ^{13}C NMR spectra of PyDMA in d_6-DMSO. One can see the three characteristic pyridine aromatic protons at 7.0 and 7.6 ppm, and the characteristic oxymethylene protons at 4.5 ppm in the ^{1}H NMR spectrum of PyDMA.

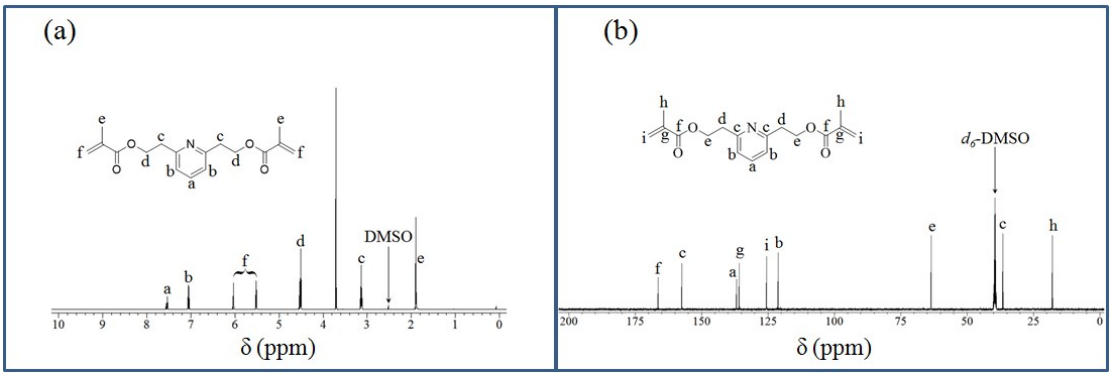

Figure S4. (a) ^{1}H and (b) ^{13}C NMR spectra of the PyDMA cross-linker in d_6-DMSO.

The theoretical structures of the three PyDMA-containing polymers prepared are listed in Table S1, which also summarizes their main characteristics. These include the DS in THF of the two polymer networks, their sol fraction (extractables), the molecular weight characteristics of the sol fraction of the networks, the molecular weight characteristics of the copolymer network after thermolysis or alkaline hydrolysis, and, finally, the molecular weight characteristics of the (soluble) hyperbranched homopolymer. The DSs in THF were found to be 1.3 and 3.1 for the homopolymer and the copolymer networks, respectively, with the lower DS value in the former case reflecting the higher cross-linking density. The sol fraction in the copolymer network was low, 6.0%. The molecular weight dispersity, *Đ*, of the hyperbranched homopolymer was rather high, at 2.13, reflecting the high branching density in this polymer. The *Đ* values of the extractables were much lower, less than 1.2, consistent with the expected lower branching density in these polymeric materials.

Table S1. Main characteristics of the three PyDMA-containing polymeric materials prepared.

Polymer Structure	DS in THF	% w/w Extract.	M_p (g mol^{-1})	M_n (g mol^{-1})	*Đ*	After Thermolysis [b]			After Alkaline Hydrolysis [c]		
						M_p (g mol^{-1})	M_n (g mol^{-1})	*Đ*	M_p (g mol^{-1})	M_n (g mol^{-1})	*Đ*
$PyDMA_{10}$	---	100	6330	5580	2.13	---	----	----	----	----	----
$PyDMA_{10}$ [a]	1.3	---	1430	1500	1.05	----	----	----	----	----	----
MMA_{100}-*co*-$PyDMA_8$ [a]	3.1	6.0	1610	1820	1.16	5710	4700	1.80	5400	6460	1.99

[a] Network formation. [b] Vacuum oven at 130 °C for 6 h. [c] NaOH (0.48 M) in DMSO at room temperature.

Figure S5 displays the ^{1}H NMR spectra in d_6-DMSO of the hyperbranched PyDMA homopolymer after staying in an acidic (DCl, 0.4 M) environment for 30 min, and also after staying in an alkaline (NaOD, 0.4 M) environment for 10, 45 and 120 min. The ^{1}H NMR spectrum of the original hyperbranched polymer is also presented in the figure for comparison. The ^{1}H NMR spectrum of the polymer in DCl (Figure S5(b)) is very similar to that of the untreated polymer, with the only difference the downfield shift of the aromatic protons, a result of the protonation of the pyridine nitrogen by the added DCl. Oxymethylene protons "d" were preserved in the spectrum, implying the stability of the ester groups in polyPyDMA. A ^{1}H NMR spectrum recorded 24 h after the addition of DCl (not presented here) was identical to the one shown in Figure S5(b), suggesting the stability of the PyDMA units in acidic conditions. This is consistent with the well-known acid-stability of the linear analogue of polyPyDMA, poly[(2-pyridin-2-yl)ethyl methacryalte] (polyPyEMA) [3].

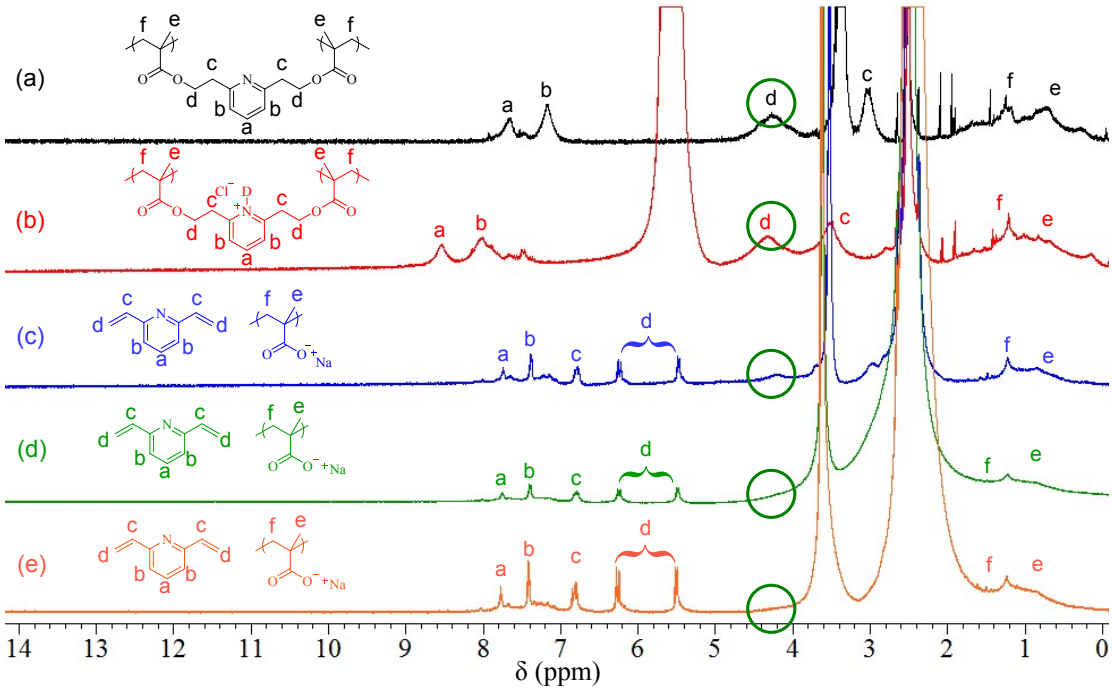

Figure S5. ^{1}H NMR spectra of the hyperbranched PyDMA homopolymer in d_6-DMSO. (a) Original polymer. (b) Polymer in acidic (DCl, 0.4 M) environment after 30 min. (c,d,e) Polymer in alkaline (NaOD, 0.4 M) environment after 10 min (c), 45 min (d), and 2 h (e).

In contrast, the treatment of polyPyDMA in alkaline conditions led to its fast hydrolysis, as manifested by the disappearance of oxymethylene protons "d" in the polymer, and the appearance of olefinic protons "c" and "d" of 2,6-divinylpyridine. Most of the sample was hydrolyzed within the first 10 min (Figure S5(c)), and hydrolysis was completed in less than 1 h (Figure S5(d)). The spectrum collected 2 h after the addition of NaOD (Figure S5(e)) was identical to a spectrum recorded after 24 h of reaction (spectrum not shown). Thus, the alkaline hydrolysis of polyPyDMA is fast, as expected from the fast alkaline hydrolysis of polyPyEMA.

The ability of polyPyDMA to be cleaved fast and selectively, under alkaline and not acidic hydrolysis conditions (and not vice versa!) is novel and important, and it may be exploited in various fields, including microelectronics and biotechnology.

Figure S6 illustrates the ^{1}H NMR spectrum of the products from the alkaline hydrolysis at room temperature of the PyDMA homopolymer network (a, black), together with the ^{1}H NMR spectrum of the thermolysis products (b, red). The ^{1}H NMR spectra of the cleavage products (*via* thermolysis or hydrolysis) in d_6-DMSO indicated the presence of olefinic protons due to the formation of 2,6-divinylpyridine, and the disappearance of the polymeric oxyethylene protons. In the thermolysis products, a weak signal due to the polyMAA carboxylic acid protons was also visible.

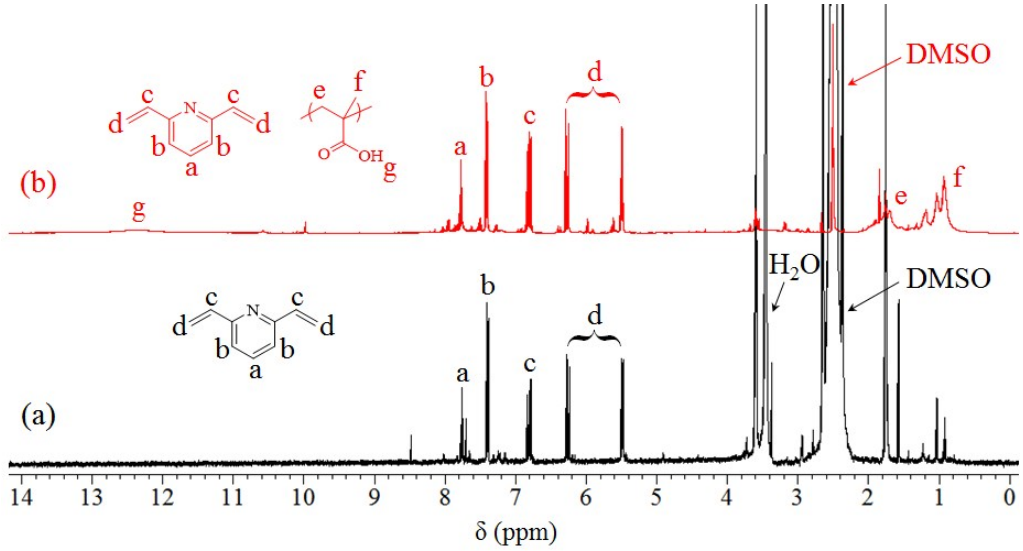

Figure S6. ^{1}H NMR spectra in d_6-DMSO of the cleavage product of the PyDMA homopolymer network (a) after alkaline hydrolysis at room temperature using NaOD in d_6-DMSO (black), and (b) after bulk thermolysis (no solvent) in a vacuum oven at 130 °C for 6 h (red).

Figure S7 presents the ^{1}H NMR spectrum of the products from the alkaline hydrolysis at room temperature of the PyDMA-MMA copolymer network (a, black), together with the ^{1}H NMR spectrum of the thermolysis products (b, red). The degradation products here were a linear MMA-MAA random copolymer plus 2,6-divinylpyridine. The signals in the ^{1}H NMR spectra were consistent with the expected degradation products.

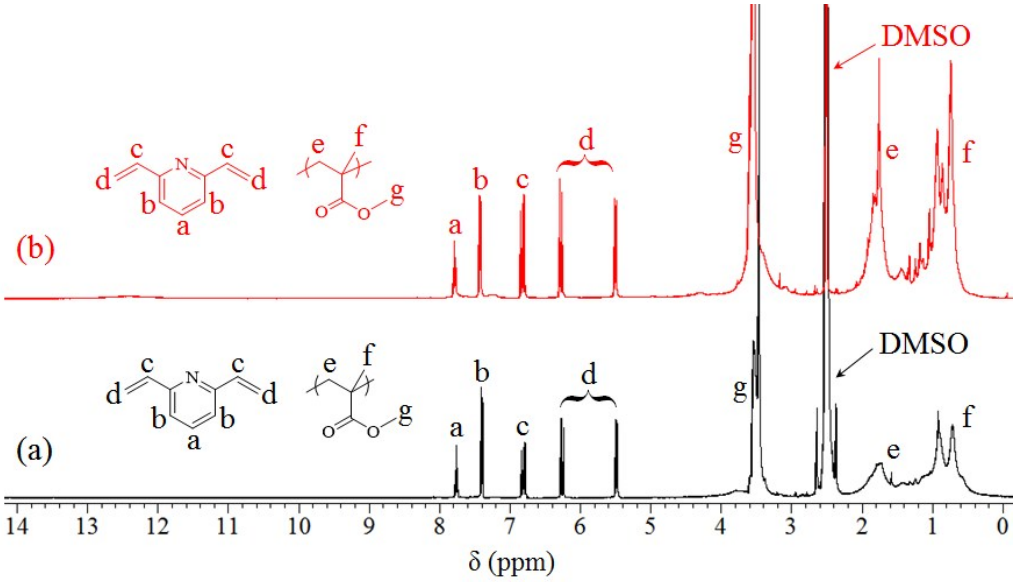

Figure S7. ^{1}H NMR spectra of the cleavage products of the PyDMA-MMA copolymer network (a) after alkaline hydrolysis using NaOD in d_6-DMSO (black), and (b) after thermolysis in a vacuum oven at 130 °C for 6 h in d_6-DMSO (red).

Figure S8 shows an overlay of the TGA traces of the three PyDMA-containing polymers. All TGA traces showed a first mass loss at 200 °C, in agreement with DSC, and a second mass loss at 400 °C due to backbone destruction. The horizontal continuous black line corresponds to the weight percentage expected to remain after complete loss of 2,6-divinylpyridine from the hyperbranched PyDMA homopolymer or the PyDMA homopolymer network, while the horizontal dashed blue line corresponds to that for the PyDMA-MMA copolymer network. In the case of the hyperbranched PyDMA homopolymer, the experimental weight loss from 200 to 350 °C agreed well with (although was slightly lower than) the calculated ("theoretical"), whereas a lower-than-calculated weight loss was observed for the PyDMA homopolymer network. Note, however, the incomplete ultimate weight removal for both PyDMA homopolymeric materials, as 12% of the initial mass still remained even

at 600 °C. This may explain the previously mentioned disagreement. In the case of the PyDMA-MMA copolymer network, the experimental weight loss slightly exceeded the calculated, possibly due to initial presence of some solvent in this sample.

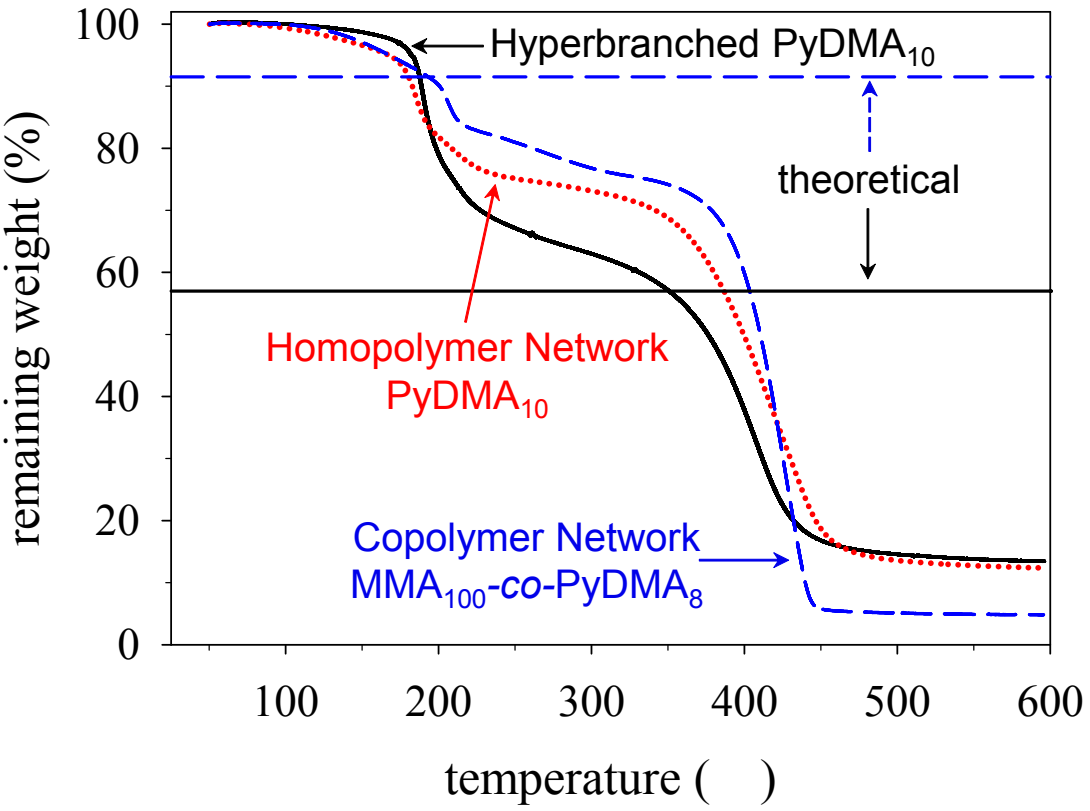

Figure S8. TGA thermograms of the PyDMA hyperbranched homopolymer (black, continuous line), the PyDMA homopolymer network (red, dotted line), and the PyDMA-MMA copolymer network (blue, dashed line).

Figure S9 displays the ATR-FTIR spectra (Shimadzu FTIR-NIR Prestige-21 spectrometer) of the PyDMA homopolymer network and the PyDMA-MMA copolymer network. In the case of the homopolymer network, a weak signal at 1630 cm^{-1} was observed, suggesting the presence of a small percentage of unreacted vinylic (methacrylate) groups. In contrast, in the case of the copolymer network, no such signal was present.

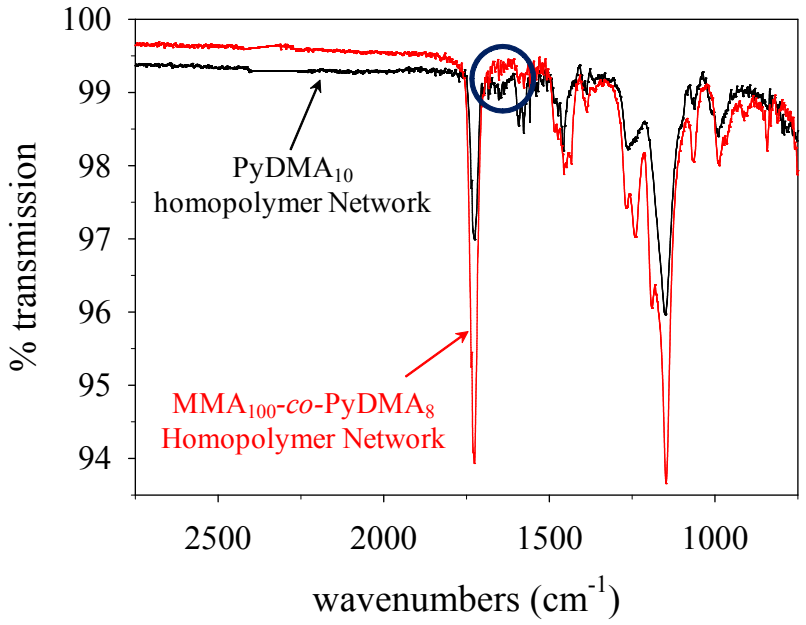

Figure S9. ATR-FTIR spectra of the PyDMA homopolymer network (black) and the PyDMA-MMA copolymer network (red).

References

1. W. S. J. Kelly, G. H. Ford and S. M. Nelson, *J. Chem. Soc. A*, 1971, 388–396.
2. K. Löffler and L. Thiel, *Chem. Berichte*, 1909, **42**, 132–140.
3. M. Elladiou and C. S. Patrickios, *Macromolecules* 2015, **48**, 7503–7512.