An easy accessible homologous set of first to fifth generation dendritic methacrylic macromonomers and their polymerizations†‡

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A practical and step-efficient synthesis of a novel homologous series of G1–G5 dendronized macromonomers and their G1–G4 polymers is described. All dendronized polymers have *tert*-butyl-protected carboxylic acid functions at the dendrons peripheries and are thus ideal candidates for subsequent "surface" engineering. In this regard they complement another existing series.

1 Introduction

Dendronized polymers are an established class of comb polymers whereby the comb's teeth are dendritic.[1] Unlike their more or less spherically shaped congeners, the dendrimers,[2] these comb polymers have an anisotropic shape which results from an increased persistence of the backbone[3] caused by the sterically demanding dendrons attached to it. For high generations and densely branched dendrons this stiffening can go as far as to render the polymers cylindrically shaped nanoobjects.[1d–f] This shape anisotropy is the key difference of dendronized polymers to dendrimers. It opens application options which include directed transport (along the cylinders),[4] hierarchical structure formation through self-assembly in bulk,[5] in solution[6] and on surfaces,[7] as well as molecular constructions on the single molecule level.[7–9] There is an increasing awareness of the potential importance of dendronized polymers and an ever increasing number of research groups are joining the field. For the applications mentioned, it would be attractive to have homologous series of dendronized polymers available which differ in dendron generation from the first to the highest experimentally feasible one. Such series would allow exploring systematically the impact of chain thicknesses, "surface" curvatures, and charge densities on, *e.g.*, torsion forces upon bending, persistence lengths, and self-assembly behaviour. Only a few homologous series of dendronized polymers involving the especially interesting fourth generation have been published by us and others.[10] Not all of them were developed to a high synthetic maturity. Others involve too tedious reaction procedures or high cost reagents. There was therefore a clear need for a new series which would provide access to dendronized polymers of at least up to the G4 level at both a reasonable effort and comparably low price. Also these polymers should, of course, carry useful functional groups in the periphery for "surface" engineering. Recently, we published a comparatively simple and "cheap" synthesis of a second generation (G2) dendronized polymer **PG2** with protected peripheral carboxylic acid functions (Fig. 1) together with a detailed molar mass determination based on gel permeation chromatography, light scattering, and analytical ultracentrifuge.[11] The corresponding data ranged between approximately 5×10^6 and 8×10^6 Da and were complemented by contour lengths determinations of spin-coated samples on solid substrates using a scanning force microscope. Because of these high molar mass values and the relatively simple chemistry involved, it was decided to develop a homologous series G1–G5 based on this G2 case. Here we describe the synthesis and purification of the corresponding G1 and G3–G5 methacrylate-based macromonomers, address the issue of their structure perfection, and describe the results of their attempted polymerizations under free radical conditions. Finally, a preliminary result regarding the reactivity of the G5 macromonomers towards the electron-rich monomer *p*-methoxystyrene will be presented. This issue relates to the well documented tendency of acceptor-substituted olefins (like the here used

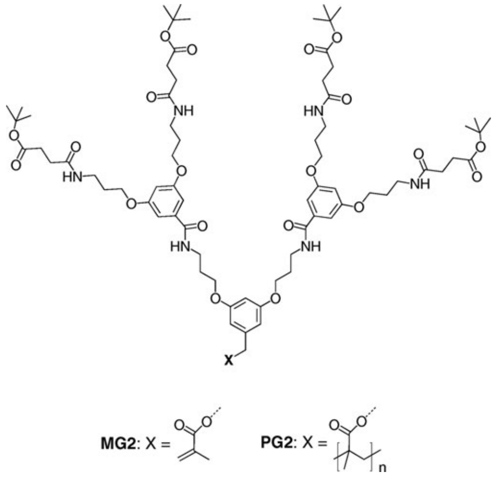

Fig. 1 Chemical structure of the second generation macromonomer **MG2** and its corresponding dendronized polymer **PG2** previously reported.[11]

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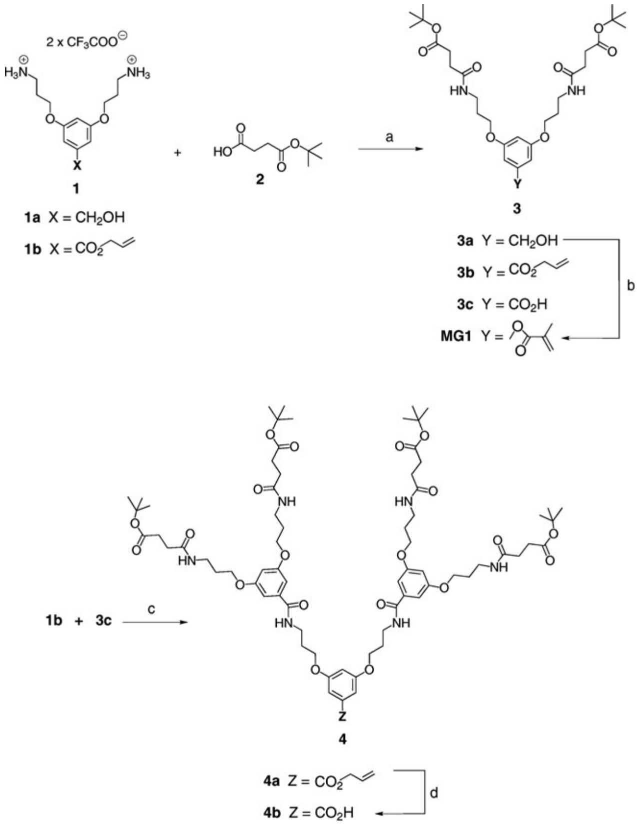
methacrylates) to give alternating copolymers with electron-rich counterparts.[12]

2 Results and discussion

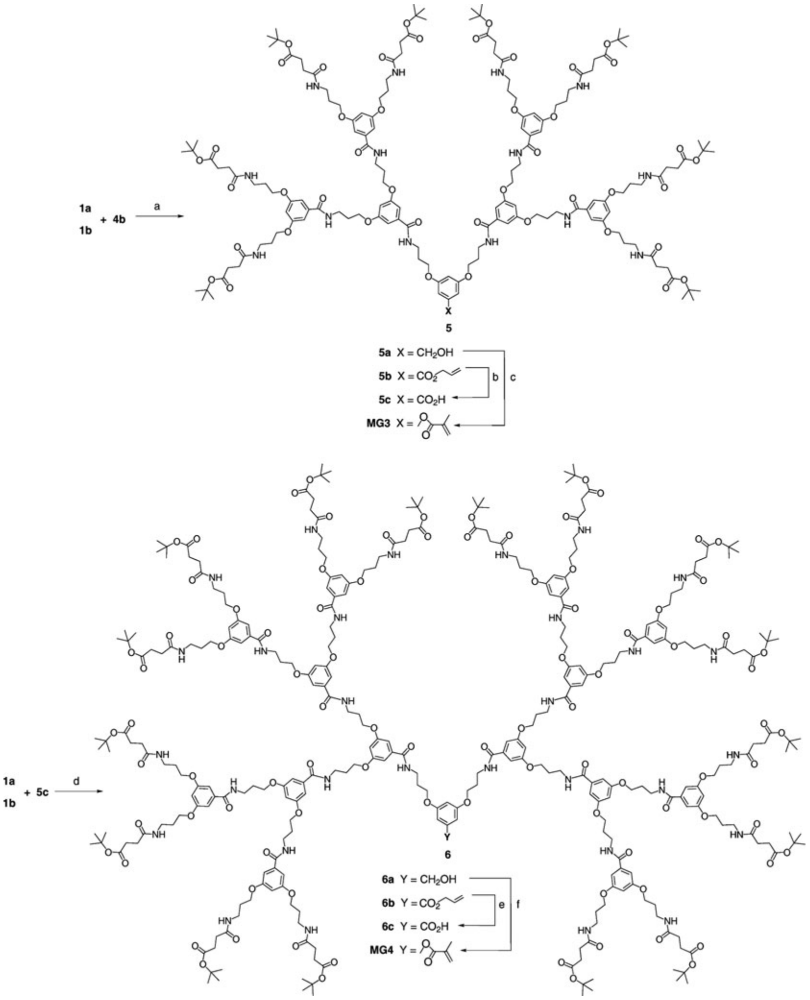
2.1 Syntheses

The synthetic steps to the G1 and G3–G5 macromonomers **MG1**, **MG3**, **MG4** and **MG5** are shown in Schemes 1–3. Their polymerizations and the deprotections of the corresponding polymers **PG1**, **PG3** and **PG4** are described in Scheme 4. All dendrons carry between two and 32 carboxylic acid *tert*-butyl-ester functions in the periphery together with a focal point allyl ester. Both esters can be independently deprotected which is a prerequisite for the construction of a first (G1) to fifth generation (G5) homologous series of dendrons as well as their corresponding macromonomers and polymers. The syntheses start from the known G1 dendrons **1a**,[13] **1b**,[13] **3b**,[11] and **3c**[11] which are easily accessible on the 100 g scale. Compound **2** was used to introduce the peripheral carboxylic acid *tert*-butyl-ester functions. The G1 macromonomer **MG1** was obtained by treating **3a** with freshly distilled methacrylic acid chloride (MAC). The latter aspect is important in obtaining high molar mass polymers. The deprotection of **3b** at its focal point to give **3c** was carried out according to the well-known Pd-catalyzed protocol for allylic esters.[14] Recrystallized Pd(0)(PPh$_3$)$_4$ was used as catalyst precursor and the deprotection proceeded at a high rate under mild conditions. This method proved efficient also for the higher generations' congeners of **3b**. The corresponding G3, G4 and G5 macromonomers **MG3**, **MG4** and **MG5** were obtained analogously to one another by using standard conditions as shown in Schemes 2 and 3. Note that the syntheses of **MG4** and **MG5** involved attaching the G3 acid **5c**, and the G4 acid **6c**, respectively, to the G1 dendron **1a**. The corresponding alcohols were then treated with MAC. This mode was chosen so as to have a fast access to these high generation macromonomers. In both cases the G3 and G4 dendrons were used in an access of 1.3–1.5 equivalents per peripheral amine group of dendron **1**. All amide forming reactions were done with hydroxy benzotriazole (HOBt) and *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDC). With increasing generation the solubility of the dendrons in non-polar solvents such as chloroform, methylene chloride and THF decreased and gel formation set in a few minutes after initially homogenous solution had formed. This process led to a precipitate poorly dispersed in a fluid phase. This may be due to formation of hydrogen bonds between ether linkages and amide functional groups that are present in the skeleton. In order to overcome eventual problems in synthesis caused by this, all the described transformations were performed in DMF–methanol solvent mixtures. Purification of all compounds was achieved by using several successive silica gel column chromatographic steps with different solvent mixtures (see ESI‡). Special care was taken of all macromonomers since previous studies had shown that their level of purity can have a considerable impact on polymerizability. Despite some losses of the material during purification, monomers **MG1**, **MG3**, **MG4** and **MG5** were obtained in 20, 3, 4 and 1.5 gram amounts, respectively, and scaling-up seems possible. All new compounds were fully characterized by high field ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and correct or almost correct data from combustion analysis (see ESI†).



Scheme 1 *Reagents and conditions*: (a) **1a**, **1b**, HOBt, EDC, DCM–MeOH, −20 °C, 16 h (70–76%); (b) **3a**, MAC, DMAP, THF, RT, 16 h (85%); (c) **1b**, **3c**, HOBt, EDC, DCM–MeOH, −20 °C, 16 h (70–76%); (d) **4a**, Pd(PPh$_3$)$_4$, $C_7H_7NaO_2S \cdot H_2O$, DCM–MeOH, RT, 4 h (85%).

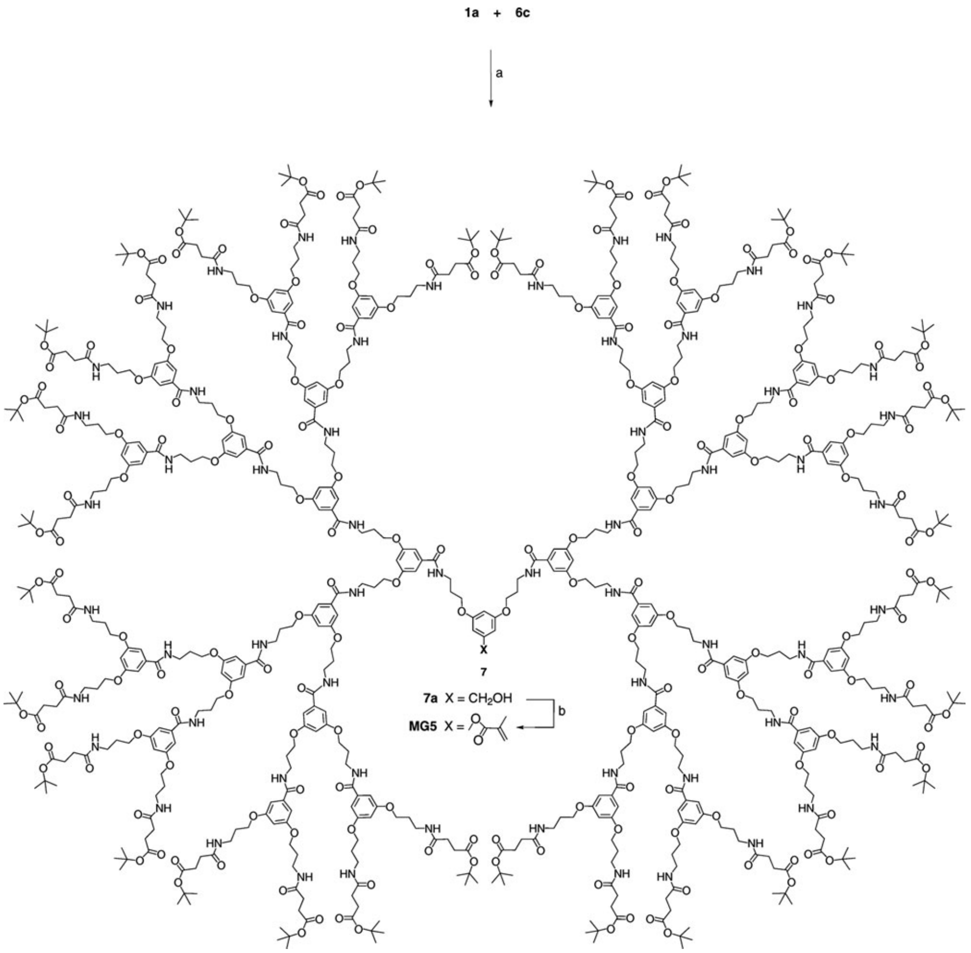
The macromonomers **MG1** and **MG3** were defect-free according to the above analytical investigations. The integrity of the higher generation macromonomers **MG4** and **MG5** was qualitatively assessed by MALDI-TOF mass spectrometry using 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene] malononitrile (DCTB) as matrix (Fig. 2 and Fig. 3). There is precedence for assessing the structural integrity of dendritic structures by mass spectrometry.[15] The spectrum of **MG4** shows the molecular ion peak at m/z 6350.7 ([M + Na]$^+$) and a low intensity signal at m/z 3393.7. The origin of this latter signal is not yet clear. Neither does it match with the assumption of an incomplete reaction between **5c** and **1a** nor can it be caused by a doubly charged species. The spectrum of **MG5** besides the molecular ion peak at m/z 12 851.4 ([M + Na]$^+$) shows two signals at m/z 6641.1 and m/z 12 782.9. The one at m/z 6641.1 can neither be straightforwardly assigned to **MG5** with one missing G4 arm nor to a doubly charged **MG5**. The signal at m/z 12 782.9 is tentatively assigned to [M + Na − ^{t}Bu]$^+$. Fig. 4 shows GPC elution curves of the monomers **MG3–MG5**. All are monomodal and the PDI values narrow (**MG3**: 1.10; **MG4**: 1.10; **MG5**: 1.12).



Scheme 2 *Reagents and conditions*: (a) **1a**, **1b**, HOBt, EDC, DMFM–MeOH, −20 °C, 20 h, (65–70%); (b) **5b**, $Pd(PPh_3)_4$, $C_7H_7NaO_2S \cdot H_2O$, DCM–MeOH, RT, 4 h (80%); (c) **5a**, MAC, DMAP, DMF, RT, 16 h (80%); (d) **1a**, **1b**, HOBt, EDC, DMF–MeOH, −20 °C, 48 h (60–65%); (e) **6b**, $Pd(PPh_3)_4$, $C_7H_7NaO_2S \cdot H_2O$, DCM–MeOH, RT, 4 h (70%); (f) **6a**, MAC, DMAP, DMF, RT, 16 h (75%).

2.2 Polymerizations

The polymerizations were done in highly concentrated yet still homogenous DMF solutions (30–50% w/w) by placing the flask into preheated baths (65 °C for **PG1** and 75 °C for **PG3**, **PG4** and the attempted **PG5**). The higher temperature for the latter experiments was chosen so as to ensure optimum stirring. 0.5–1.5 mol% of recrystallized AIBN were used as initiator precursor. In the case of **PG1** the initially clear and homogenous solution after 2–3 h showed a viscosity increase, and polymerizations were continued for another 8–10 h when the mixture had completely solidified. Precipitation in methanol–water mixtures furnished a colorless, amorphous solid in 75–90% yield after freeze-drying. Polymers **PG3** and **PG4** were obtained similarly except for longer reaction times (2 d instead of 16 h) and the high temperatures mentioned. For them, purification was done by repeated chromatography through short silica gel columns using DCM as eluent prior to precipitation. For each generation of macromonomer several polymerization experiments were performed thus confirming the reproducibility. The polymerization of **MG5** was tried several times by employing up to 1 g of monomer. In no case polymer could be obtained; only unchanged monomer was recovered. Relevant conditions and results are summarized in Table 1. The molar mass data were obtained by GPC in DMF (with 1 g L^{-1} LiBr) at 80 °C using a PMMA standard for calibration based on two-angle light-scattering, viscometry and refractive index detectors. Fig. 5 shows typical GPC elution curves for **PG3** and **PG4** together with the already published **PG2**. As can be seen from the data in Table 1 the weight average degrees of polymerization (P_w) decrease as the dendron generation increases. Whereas for **PG1** the accessible chain lengths are basically ‘‘unlimited’’, for **PG2–PG4** P_w values are to be expected in the range of 2500–5000 (**PG2**), 700–1300 (**PG3**) and 10–50 (**PG4**). Though conversion can still be high, there is a trend towards sharply decreasing chain lengths with increasing dendron generation. Even though the molar masses given here tend to underestimate the actual values, the present series does not provide access to significantly longer high generation dendronized polymers than a previous one[10d] despite its less tight dendritic structure. As pointed out earlier, whenever long chains of high generation polymers are needed, a mixed strategy which combines the macromonomer with the attach-to approach is the method of



Scheme 3 *Reagents and conditions*: (a) **1a**, HOBt, EDC, DMF–MeOH, −20 °C, 48 h (60%); (b) **7a**, MAC, DMAP, DMF, RT, 16 h (60%).

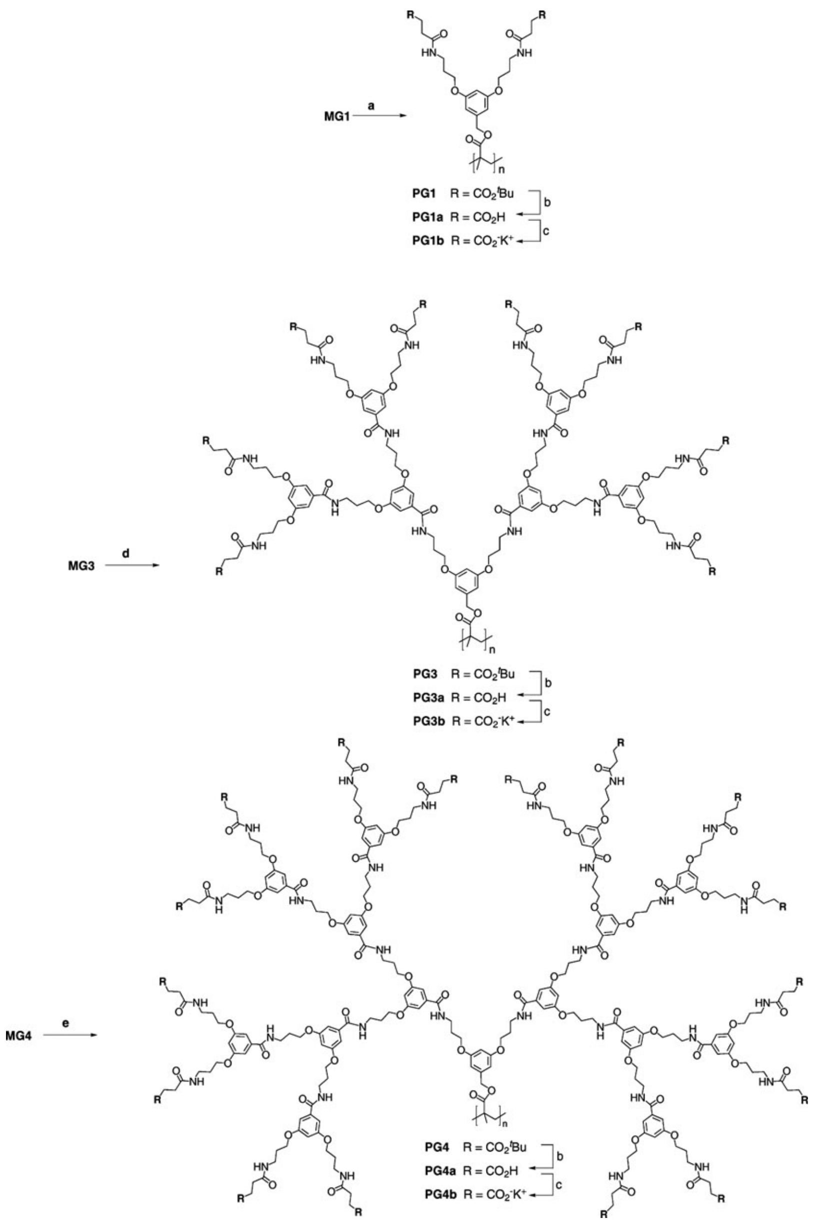
choice.[10c] The polydispersities are sometimes broader than expected.

In an attempt to check whether the polymerizable group of **MG5** can at all be reached by other monomers, 1 equivalent of it was reacted with 100 equivalents of the simple and electron-rich *para*-methoxystyrene in the presence if 0.16 mol% AIBN at 65 °C for 18 h (reaction not shown).[12] The ^{1}H NMR spectrum of the precipitated polymer formed, in fact, showed signals due to the incorporation of both monomers. The structural analysis has not yet been completed; the degree of alternance in this copolymer seems to be low.

Thermogravimetric analyses proved the polymers **PG1–PG4** to be thermally stable up to 214 °C followed by an abrupt and complete loss of *tert*-butyl groups. The glass transition temperatures were determined by differential scanning calorimetry (DSC) for the homologous series of protected polymers (**PG1–PG4**) (Fig. 6) and their respective deprotected and negatively charged counterparts (**PG1b–PG4b**) (Fig. 7). The DSC curves shown were obtained after one completed heating and cooling cycle and exhibit clear glass transitions which are as follows (in °C): **PG1**: 41, **PG2**: 52[11] **PG3**: 53, **PG4**: 60, **PG1b**: 105, **PG2b**: 124, **PG3b**: 102, and **PG4b**: 107. As is normally observed, the T_g values for the charged polymers were higher than that of their non-charged analogs. For the neutral series the values steadily increase with generation and in absolute terms are comparable to earlier reported ones of structurally related dendronized polymers.[5c] For the charged series there is no clear trend. Further investigations would be required to explain this behaviour.

3 Conclusions

A new homologous series of dendronized macromonomers, **MG1–MG5**, has been developed which holds great promise because of its ease of synthetic access and the greatly reduced costs associated with its preparation compared to a structurally related series published a few years back.[10d] The synthesis of monomers **MG1** and **MG2** has meanwhile been further scaled-up to the 500 and 300 g scale, respectively,[16] which will allow for significantly larger quantities of the higher generation homologs to be prepared. The monomers **MG1–MG3** are structurally perfect. The two higher homologs **MG4** and **MG5** may have subtle structural defects which were discovered by MALDI-TOF mass spectrometry, but which could not be assigned yet with certainty. One defect is tentatively explained in terms of loss of one of the many peripheral *tert*-butyl groups which, thus, does not interfere with the main skeleton's structural integrity. The monomers **MG1–MG4** in the presence of AIBN polymerize to the corresponding high molar mass polymers **PG1–PG4** whereby, however, the number of



Scheme 4 *Reagents and conditions*: (a) AIBN, DMF, 65 °C, 24 h (90%); (d) & (e) AIBN, DMF, 75 °C 48 h, (85–90%); (b) TFA, RT, 24 h (95%); (c) KOH, MeOH, RT, 3 h.

repeat units decreases with increasing generation. Typical P_w values for **PG4** are in the range of 30–50 whereas for **PG3** still values of P_w = 1000 can be achieved. This behaviour is typical for dendronized macromonomers if not for macromonomers in general. It is therefore not too surprising that the spatially by far most demanding monomer **MG5** could not be homopolymerized despite a number of attempts. Nevertheless, a first orienting experiment proves that **MG5** can be used for copolymerizations, at least with the electron-rich *para*-methoxystyrene.[12] The polymers described in this paper enables one to more easily explore the class of dendronized polymers both under fundamental and applied aspects. The negatively charged **PG1b–PG4b** will be of special interest as counterparts to positively charged dendronized polymers for studies of homo and hybrid supramolecular assemblies.

4 Experimental

Compounds **1a**,[13] **1b**,[13] **3b**[11] and **3c**[11] were synthesized according to literature methods. Details of the synthesis and characterization of the new compounds are given in the ESI. Other reagents were purchased from Aldrich, Acros, Fluka or Synwit Technol., Beijing. Methacryloyl chloride (MAC) was freshly distilled before use. Tetrahydrofuran (THF) and triethylamine (TEA) were refluxed over Na with benzophenone as indicator, dichloromethane (DCM) was dried by distilling over CaH_2. All other reagents and solvents were used as received. All reactions were performed under nitrogen atmosphere.

Silica gel 60 M (Macherey-Nagel, 0.04–0.063 mm/230–400 mesh) was used as the stationary phase for column chromatography. Whenever possible, reactions were

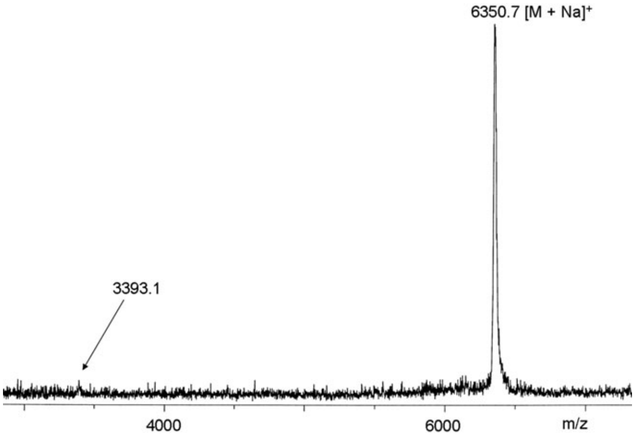


Fig. 2 MALDI-TOF mass spectrum of macromonomer **MG4** to qualitatively assess its degree of structure perfection. The signal at *m*/*z* 3393.1 could not yet be assigned.

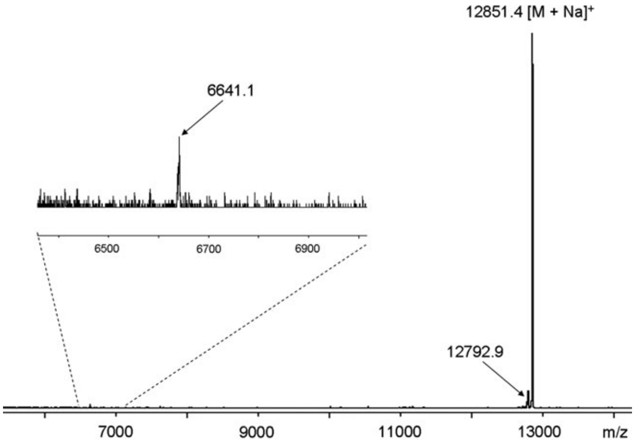


Fig. 3 MALDI-TOF mass spectrum of macromonomer **MG5** to qualitatively assess the degree of structure perfection. The signal at *m*/*z* 6641.1 can neither be straightforwardly assigned to a G5 monomer with one missing G4 arm nor to a doubly charged **MG5**. The signal at *m*/*z* = 12 782.9 is tentatively assigned to [M + Na – ^{t}Bu]$^+$.

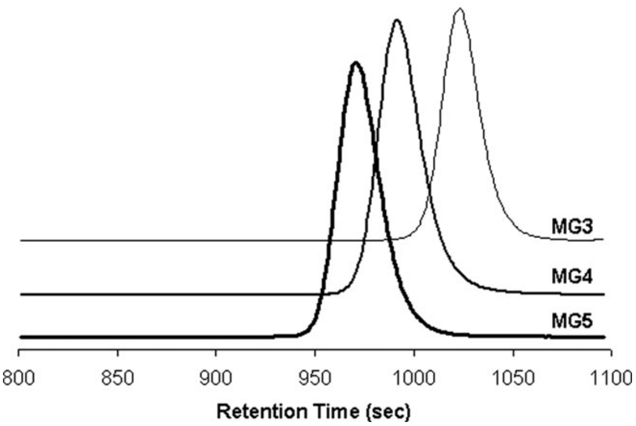


Fig. 4 GPC elution curves of macromonomers **MG3–MG5** in DMF (with 1 g L^{-1} LiBr) at 80 °C as an indication of purity. For PDI values, see text.

monitored by thin-layer chromatography (TLC) using TLC silica gel coated aluminium plates 60F$_{254}$ (Merck). Compounds were detected by UV light (254 or 366 nm) and/or by treatment with a solution of ninhydrin in ethanol followed by heating.

If not otherwise noted, ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz) and AV 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) spectrometers at room temperature using chloroform-d as a solvent if not otherwise stated.

High-resolution mass spectral (HRMS) and ESI-MS analyses were performed by the MS-service of the Laboratorium für Organische Chemie at ETH Zürich. ESI-MS and MALDI-MS were run on an IonSpec Ultra instrument. In the case of MALDI-MS, 2,5-dihydroxybenzoic acid (DHB), 2-[(2*E*)-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) or 3-hydroxypyridine 2-carboxylic acid (3-HPA) served as the matrix. The FAB experiments were carried out with 3-nitrobenzyl alcohol (MNBA)–CH$_2$Cl$_2$.

Elemental analyses were performed by the Mikrolabor of the Laboratorium für Organische Chemie, ETH Zürich. The

Table 1 Conditions for and results of radical polymerization of monomers **MG1**, **MG2**, **MG3**, **MG4** and **MG5**

Entry	Monomer	Amount/g	DMF/μL	AIBN (mol%)	Time/h	Yield (%)	$10^{-6}M_n{}^a$	$10^{-6}M_w{}^a$	$P_w{}^a$	PDI^a
1	**MG1**	0.19	100	0.3	16	75	0.80	3.72	5860	4.68
2	**MG1**	0.14	75	0.4	16	75	0.49	3.40	5387	7.01
3	**MG1**	0.21	115	1.0	16	80	0.33	3.56	5718	10.7
4	**MG2**	0.21	70	0.6	16	85	1.11	4.51	3116	4.04
5	**MG2**	0.23	80	0.8	16	78	1.23	3.76	2598	3.04
6	**MG2**	0.44	150	0.8	16	78	1.39	4.34	2999	3.12
7	**MG2**	1.00	450	1.0	16	87	2.73	7.42	5127	2.71
8	**MG2**	2.22	1000	0.7	16	90	2.91	8.47	5850	2.91
9	**MG3**	0.71	325	1.5	24	30	0.46	2.54	826	5.52
10	**MG3**	1.00	550	1.5	24	25	1.41	3.99	1300	2.82
11	**MG3**	0.50	300	1.5	48	25	0.82	2.83	920	3.45
12	**MG3**	0.50	200	2.6	48	78	1.01	2.07	673	2.04
13	**MG3**	0.70	300	2.4	48	80	0.33	0.80	260	2.42
14	**MG4**	2.26	910	2.0	48	82	0.18	0.32	50	1.77
15	**MG4**	1.10	236	2.0	48	20	0.01	0.06	10	4.79
16	**MG4**	0.37	110	1.5	48	52	0.10	0.28	44	2.82
17	**MG5**	1.00	400	2.0	48	0	—	—	—	—

[a] Triple detector GPC calibrated with PMMA standards in DMF at 80 °C.

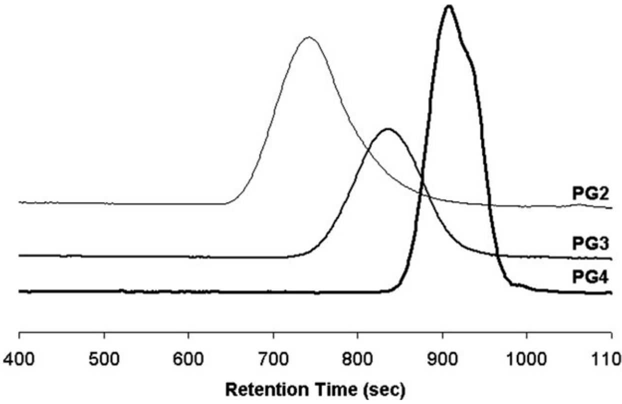


Fig. 5 GPC elution curves of polymers **PG2**[11]–**PG4** in DMF (with 1 g L^{-1} LiBr) at 80 °C.

samples were dried rigorously under vacuum prior to analysis to remove strongly adhering solvent molecules. Nevertheless for all deprotected polymers with carboxylic acid functions (**PG1a**, **PG3a**, **PG4a**) correct values could not be obtained.

Gel permeation chromatography (GPC) measurements were carried out using PL-GPC 220 instrument with 2x PL-Gel Mix-B LS column set equipped with RI (refractive index), viscosity and LS (Light Scattering with 15 and 90° angle) detectors [DMF + 1 g L^{-1} LiBr as eluent at 80 °C]. Universal calibration was done using PMMA standards in a range of M_p = 2680 to 3 900 000 (Polymer Labs. Ltd, UK).

High-resolution thermogravimetric analysis (TGA) was performed on a Q500 thermogravimetric analyzer (TA Instruments, New Castle, DE, USA). All measurements were carried out in an air stream under the same conditions. The mass loss was plotted against increasing temperature as well as its first derivative (DTG) that represents the change in decomposition rate. The differential scanning calorimetry (DSC) was carried out under nitrogen at a heating or cooling rate of 10 °C min^{-1} on a DSC 7 (Perkin-Elmer, Norwalk, CT). Two heating and one cooling run were consecutively carried out in a cycle and the peak maxima were considered as the transition temperatures.

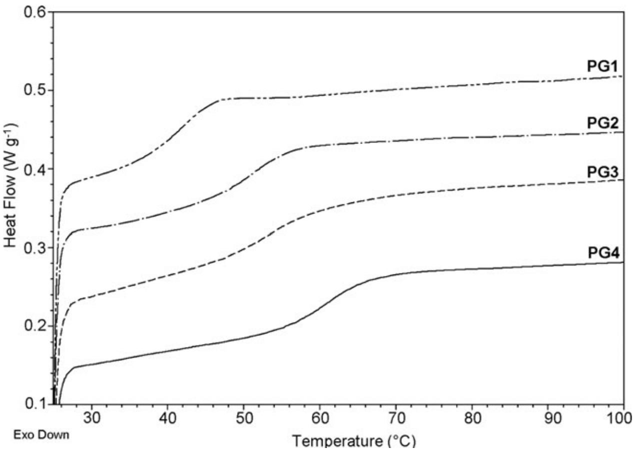


Fig. 6 TGA curves of **PG1–PG4** after a completed heating/cooling cycle (heating rate: 10 °C min^{-1}, under nitrogen).

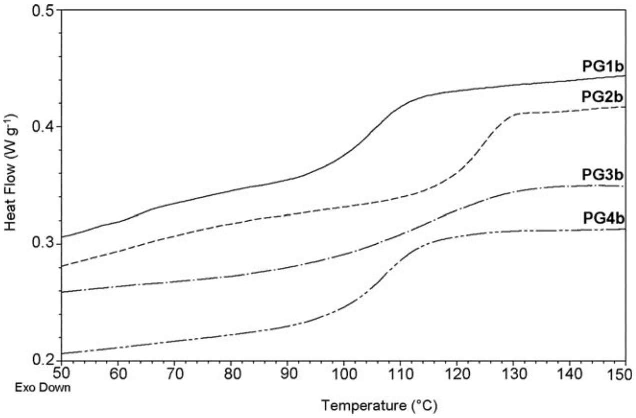


Fig. 7 TGA curves of the potassium salts **PG1b–PG4b** after a completed heating/cooling cycle (heating rate: 10 °C min^{-1}, under nitrogen).

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