Efficient Synthesis of High Molar Mass, First- to Fourth-Generation Distributed Dendronized Polymers by the Macromonomer Approach

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Abstract: A homologous series of first- to fourth-generation (G1–G4) dendronized macromonomers, **5**, **7**, **10**, and **12**, was synthesized, and their polymerization behavior under radical conditions investigated. These conditions were thermally induced radical polymerization (TRP) and atom-transfer radical poymerization (ATRP). TRP was applied to all monomers and gave polymers **PG1**–**PG4**, whose molar masses range from several millions for **PG1** to estimated several hundreds of thousands for **PG2** and **PG3**, and to the oligomeric regime for **PG4**. ATRP was applied only to the G1 and G2 monomers **5** and **7**. Kinetic studies on monomer **5** provide evidence that its polymerization proceeds in a controlled fashion. The highest monomer-to-initiator ratios which still gave monomodal molar mass distributions were 300:1 (for **5**) and 100:1 (for **7**), which correspond to achievable molar mass regime for **PG1** and **PG2** of approximately $M_n = 100\,000$ (DP_{calcd}(**PG1**) = 200, DP_{calcd}(**PG2**) = 90). The polydispersities lie in the usual range (PDI = 1.1–1.2). The molar masses were determined by GPC in DMF with calibration against absolute molar masses of **PG1** determined by light scattering.

Keywords: dendrimers · dendronized polymers · macromonomers · polymerization · radical polymerization

Introduction

The dendronization of polymer chains at each repeat unit with increasingly voluminous dendrons has led to new comb macromolecules which are referred to as dendronized polymers.[1] The unusual structure of these polymers with their tight and highly branched layer around the backbone has raised fundamental questions in polymer science, which all have their origin in the influence of the layer on the conformation and rigidity of the backbone.[2] It has also opened the way to unprecedented applications of certain representatives in relation to the bottom-up approach to nanosciences, in which dendronized polymers are used as individual nanoobjects.[3] A quasihomologous series of first- to fourth-generation (G1–G4) polymers proved to be specifically successful here, because it allowed systematic, generation-dependent study of certain phenomena. This series was made available on a 0.5–1 g scale per representative.[4] It was obtained by conventional free-radical polymerization of G1 and G2 dendronized macromonomers followed by generation-by-generation buildup with G1 dendrons until the final, fourth generation was reached. Because of this mode of synthesis the representatives of this series had virtually the same degree of polymerization and distribution, whereby the latter was relatively broad. Controlled radical polymerizations were recently developed to the point where narrowly distributed materials are now available for a number of monomers, most of which are simple styrenes and acrylates.[5] A good example of this is so-called atom-transfer radical polymerization (ATRP), in which transition-metal halides are used to activate the carbon atom of a carbon—halogen bond long enough for radical attack on a monomer and short enough to undergo termination.[5,6]

To investigate the broader potential, including areas where commercial polymers are mostly used instead, easy synthetic access to high molar mass and reasonably narrowly distributed dendronized polymers was needed. Such a goal included avoidance of the relatively laborious attach-to buildup procedure, irrespective of its remarkably high degree of structure control. We describe here novel and optimized routes to methacrylate-based G1–G4 dendronized macromonomers without spacers between the polymerizable group and dendron that involve only a few high-yield steps which give analytically pure materials on 20–30 g (G1 and G2) and 2–4 g scales (G3 and G4). The "spontaneous" (thermally induced) polymerization (TRP) and ATRP of the G1

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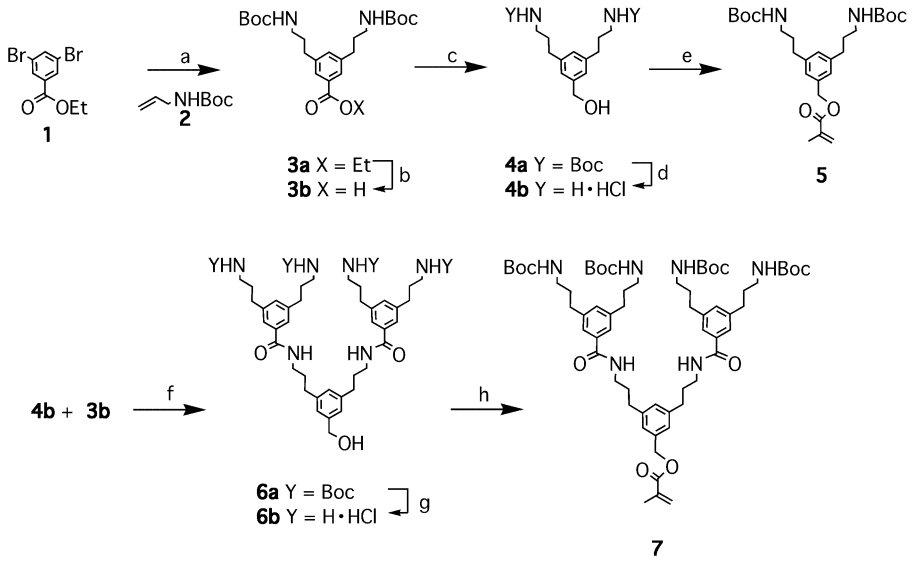
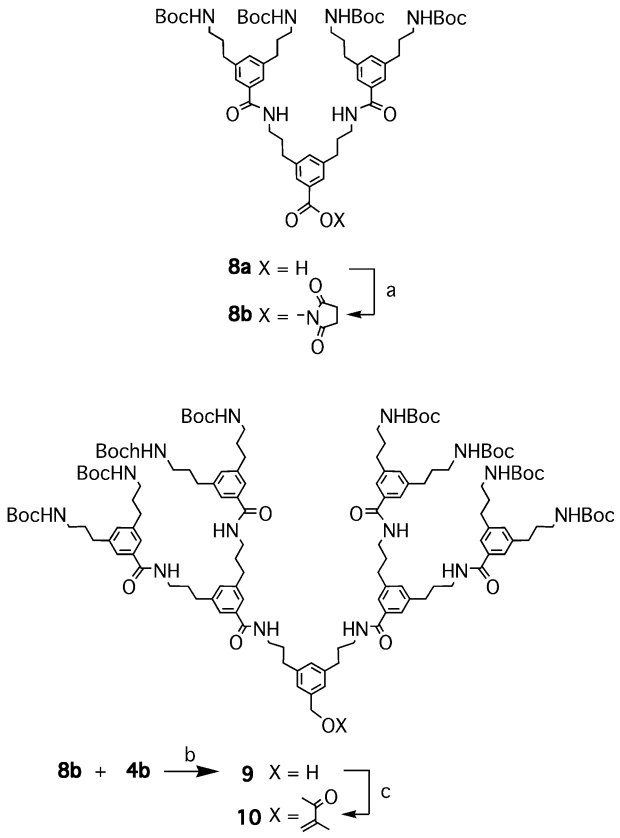
monomer to the corresponding polymer **PG1** are delineated in detail, and respective advantages and disadvantages of these methods are compared. Polymerizations of other monomers under TRP conditions provide a comprehensive picture of what can be achieved with such monomers in dependence on their generation. A few experiments were also conducted with the radical initiator bis(*tert*-butylcyclohexyl) peroxocarbonate (BCPC). Finally an in-depth molar mass determination of **PG1** is presented.



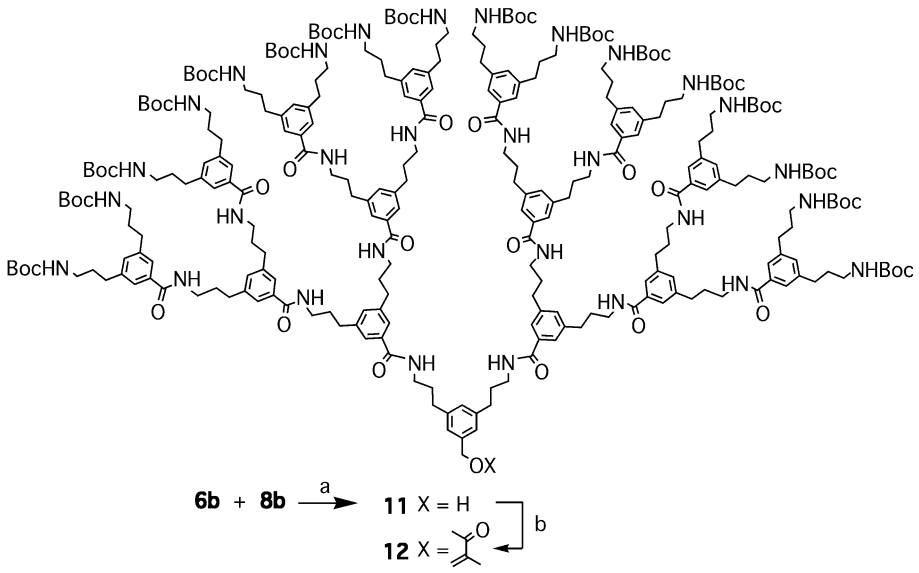
Scheme 1. Reagents and conditions: a) 1. **2**, 9-borabicyclo[3.3.1]nonane, toluene, 0 °C, 12 h (96 %); 2. 1 M KOH, **1**,]Pd(PPh$_3$)$_4$], 100 °C, 10 h (86 %); b) **3a**, KOH, 55 °C, 10 h (92 %); c) **3a**, LAH, THF, 0 °C, 16 h (93 %); d) **4a**, 25 % HCl, THF, 0 °C, 4 h (96 %); e) **4a**, MAC, DMAP, TEA, THF, 0 °C, 12 h (94 %); f) 1. **3b**, HOBt, EDC, DCM, −30 °C, 3 h; 2) **4b**, TEA, DCM, MeOH, −20 °C, 14 h (65 % for both steps); g) **6a**, 25 % HCl, THF, 0 °C, 4 h (97 %); h) **6a**, MAC, DMAP, THF, RT, 12 h (96 %).

Results and Discussion

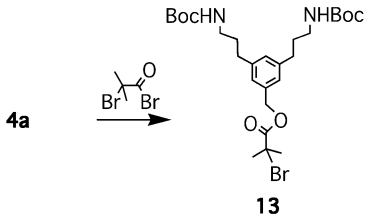
Monomers: The spacerless[7] G1–G4 macromonomers **5**, **7**, **10**, and **12** were selected for this study. Given the experience with structurally related monomers[8] they ought to be easily and reasonably accessible. Additionally, they carry functional groups at the dendron termini, which at a later stage allows the "surfaces" of the resulting polymers to be engineered for various applications. Synthesis of **5** and **7** starts with the known step[8] from dibromobenzoic ester **1** to branching unit **3a** (Scheme 1), which was scaled up here to the degree that **3a** is now available on a 100 g scale. Reduction of **3a** with lithium aluminum hydride (LAH) in THF afforded alcohol **4a** in 93 % yield. In diethyl ether the yield dropped to 35 %.[9] Compound **4a** represents a dividing point on the route to two monomers. Monomer **5** was obtained directly by treating **4a** with freshly distilled methacrylic acid chloride (MAC). For monomer **7**, **4a** was first deprotected with hydrochloric acid to give **4b**, the free amino groups of which were coupled to acid **3b** with standard peptide methods involving hydroxybenzotriazole (HOBt) and *N*-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC) to give G2 alcohol **6**, which was treated with MAC to yield **7**. Here the use of freshly distilled MAC proved important as far as maximum molar masses of the corresponding polymers was concerned. Both syntheses were carried out several times and can be considered optimized. Their efficiency is illustrated by the overall yields of 75 % (**5**) and 48 % (**7**) and the fact that both macromonomers are obtainable on a 20–30 g scale per run as analytically pure material. The corresponding G3 and G4 monomers **10** and **12** were respectively obtained by standard procedures, as shown in Schemes 2 and 3. Purification was achieved by column chromatography and was associated with some losses of material. Thus, monomer **10** was obtained in a yield of 53 % (from **8a**) and monomer **12** in 30 % (from **6b**). Finally, the ATRP initiator **13** was prepared according to Scheme 4. All new compounds were fully characterized by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and correct or almost correct data from combustion analysis.



Scheme 2. Reagents and conditions: a) **8a**, HOSu, DCC, DCM, −20 °C, 12 h (98 %); b) 4b, **8b**, TEA, MeOH, DCM, 12 h (91 %); c) **9**, MAC, TEA, DMAP, THF, 0 °C, 12 h (84 %).



Scheme 3. Reagents and conditions: a) **6b**, **8b**, TEA, DCM, MeOH, −30 °C, 12 h (82 %); b) **11**, MAC, DMAP, TEA, THF, 0 °C, 12 h (82 %).



Scheme 4. Reagents and conditions: **4a**, TEA, DMAP, 2-bromoisobutyryl bromide, THF, RT, 12 h (90 %).

Polymerization: Two polymerization methods were applied: 1) an inadvertent "spontaneous" polymerization, referred to as thermally induced radical polymerization (TRP), and 2) atom-transfer radical polymerization (ATRP) according to Matyjaszewski's procedure.[5,6] A few experiments were also performed with the conventional radical initiator BCPC. TRP was applied to monomers **5**, **7**, **10**, and **12**, and ATRP to monomers **5** and **7**. TRP was observed repeatedly during large-scale purification procedures, specifically when the solvent was removed in vacuo while heating the flask externally to 55 °C. For ATRP, pentamethyldiethylenetriamine (PMDETA) proved to be the best ligand for copper(I) bromide, after the alternative ligands 2,2′-bipyridyl and 1,1,4,7,10,10-hexamethyltriethylenetetramine had been briefly screened. Some representative results of the numerous polymerization experiments performed for monomers **5** and **7** to furnish polymers **PG1** and **PG2**, respectively, are listed in Tables 1 and 2. Table 1 also lists a few representative results for the higher generation monomers **10** and **12**. All these experiments were typically performed on a 0.5 g scale for TRP, and on a 2 g scale for ATRP. Tables 1 and 2 list the results for TRP and ATRP, respectively. Figure 1 a and b depict GPC elution curves for some entries in Tables 1 and 2, respectively. So far we have no explanation for the multimodal GPC traces (curves 4 in Figure 1 a and b). Curve 4 in Figure 1 a originates from thermal polymerization of **12** in DMF and shows only oligomeric species. In contrast, the ATRP product of **7** (curve 4, Figure 1 b) exhibits a complex GPC trace which covers the whole separation range from the upper exclusion limit down to oligomeric species. To exclude overloading effects, measurements were repeated for concentrations which differ by a factor of 10 (i.e., 1 g L^{-1} and 10 g L^{-1} injection concentration). However, the GPC traces did not change at all. Alternatively, there is the possibility of anomalous elution, as discussed in more detail below, which is known to occur in very large polymers or aggregating systems. For the present samples we have no evidence that the GPC results are significantly affected by such an anomaly, which, however, can only be detected by GPC-MALLS (MALLS = multi angle laser light scattering) coupling. GPC-MALLS in DMF was not yet successful in our lab, because particles of 50 nm to 100 nm in

Table 1. Conditions and results for radical polymerization (TRP and FRP) of monomers **5**, **7**, **10**, and **12**.

Entry	Monomer	Conditions[a]				GPC (**PG1**)[b]			GPC (PMMA)[c]	
		[I] [mmol L^{-1}]	[M] [mmol L^{-1}]	Time [h]	Yield [%]	$10^{-4} M_n$	PDI	DP_n	$10^{-4} M_n$	PDI
1	**5**	0	bulk	1.5	75	56.8	2.02	1158	24.2	1.97
2	**5**	0	bulk	3	78	69.5	3.41	1417	30.0	3.19
3	**5**	0	bulk	8	86	190.4	3.13	3881	83.5	2.78
4	**5**	0	0.82	28	75	129.4	3.69	2637	57.9	3.26
5	**5**	0	1.02	18	80	124.1	4.04	2529	52.4	3.76
6	**5**	0	1.36	5.5	78	150.8	4.26	3074	65.1	3.80
7	**5**	0	1.36	18	89	147.0	4.16	2996	62.0	3.83
8	**7**	0.89[d]	0.30	72	83	24.1	2.20	214	10.4	2.16
9	**7**	1.48[d]	0.30	72	86	24.0	1.99	213	10.3	1.97
10	**7**	2.96[d]	0.30	72	85	16.7	5.94[e]	148	7.7	5.37[e]
11	**7**	0	0.30	72	79	21.4	2.28	190	9.2	2.24
12[f]	**7**	0	0.60	26	75	67.3	3.33	597	28.8	3.14
13[f]	**7**	0	0.60	48	86	73.0	3.39	647	31.1	3.20
14[f]	**10**	0	0.30	30	50	81.9	3.97	341	34.5	3.72
15[f]	**12**	0	0.14	48	88	15.0	1.61	30	6.1	1.62

[a] In benzene at 55 °C. [b] Calibrated with light-scattering data. [c] Calibrated with PMMA standard. [d] BCPC as initiator. [e] Multimodal. [f] In DMF at 55 °C.

Table 2. Conditions and results for ATRP of monomers **5** and **7** at 55 °C in toluene.

Entry	Monomer	Conditions[a]				GPC (**PG1**)[c]			GPC (PMMA)[d]		
		[M]/mol L^{-1} [mmol L^{-1}]	[M]:[**13**]	Time [h]	Yield [%]	$10^{-4} M_{n,calcd}$[b]	$10^{-4} M_n$	PDI	DP_n	$10^{-4} M_n$	PDI
1	**5**	1.02	50:1	20	92	2.3	4.6	1.56	94	2.5	1.34
2	**5**	1.02	100:1	0.16	55	2.7	5.7	1.12	116	2.7	1.08
3	**5**	1.02	100:1	0.5	69	3.4	6.5	1.15	132	3.1	1.11
4	**5**	1.02	100:1	1.0	81	4.0	6.9	1.14	141	3.2	1.11
5	**5**	1.02	100:1	2.0	85	4.2	7.0	1.15	143	3.2	1.11
6	**5**	1.02	100:1	4.5	86	4.2	7.5	1.13	153	3.5	1.10
7	**5**	1.02	100:1	15	93	4.6	9.2	1.28	188	4.2	1.24
8	**5**	1.02	300:1	16	92	13.5	20.9	1.21	426	9.0	1.20
9[e]	**5**	1.02	100:1	24	86	4.2	8.9	1.34	181	4.1	1.25
10[e]	**5**	1.02	300:1	24	87	12.8	7.0	1.23	143	3.3	1.17
11	**7**	0.45	100:1	48	86	9.7	12.0	1.28	106	5.3	1.25
12	**7**	0.45	200:1	48	85	18.0	10.8	8.74[f]	96	5.1	7.51[f]
13	**7**	0.45	300:1	48	84	28.4	13.3	2.69[f]	118	6.0	2.54[f]

[a] [PMDETA]:[CuBr]:[**13**] = 3:1:1. [b] $M_{n,calcd}$ = yield × molar mass of monomer × [M]:[**13**]. [c] Calibrated with light-scattering data. [d] Calibrated with PMMA standard. [e] 90 °C. [f] Multimodal.

size were permanently eluted, which most probably originate from the packing material.

Absolute calibration of GPC for the G1 polymers in DMF: The absolute molar masses of some selected samples from Tables 1 and 2 were determined by light scattering (LS; for details, see below), and the values obtained used for GPC calibration (Table 3). An absolute calibration curve was established by an iteration procedure utilizing the experimental peak retention times and identifying the initial peak molar masses with M_w. With this calibration

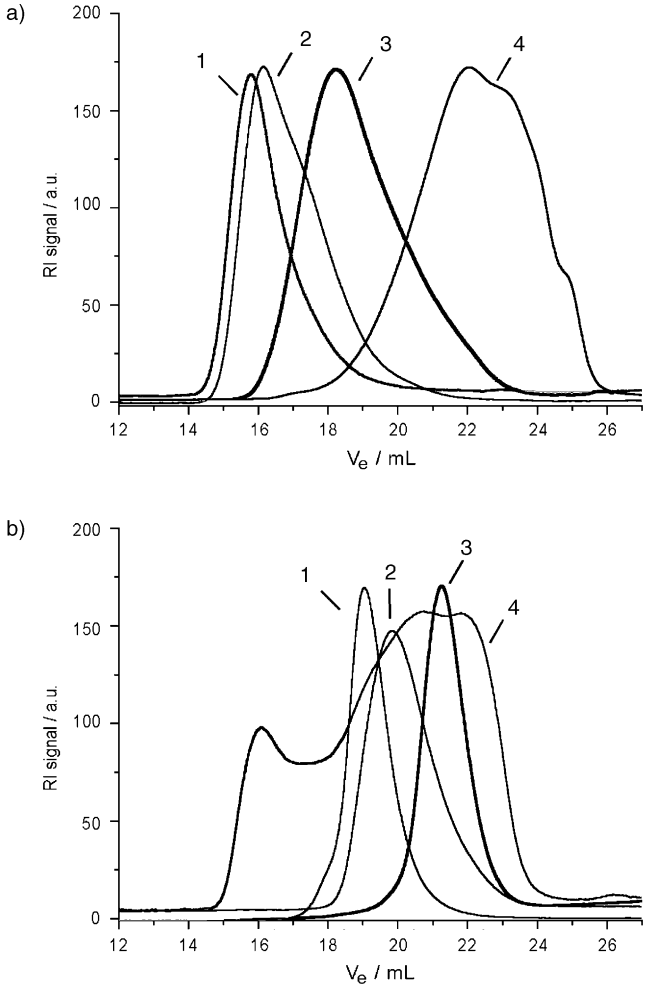


Figure 1. GPC elution curves (1–4) of a) **PG1**–**PG4** samples of Table 1 (1: entry 6; 2: entry 14; 3: entry 11; 4: entry 15) obtained by thermally induced and free-radical polymerization and b) **PG1** and **PG2** samples of Table 2 (1: entry 8; 2: entry 11; 3: entry 6; 4: entry 12) prepared by ATRP.

Table 3. Light-scattering and GPC data in DMF utilizing the absolute calibration curve as described in the text for some selected **PG1** samples.

Table	Entry	$10^{-6} M_w$ (GPC) [g mol^{-1}]	$10^{-6} M_w$ (LS) [g mol^{-1}]	$R_{g,z}$ [nm]
2	7	0.118	0.116	–
			0.10[a]	–
2	8	0.253	0.287	13.3
			0.250[a]	(12.0[a])
1	1	1.147	1.14	26.7
1	2	2.37	2.3	44.6
1	7[b]	(4.77)	(22.5)	(217)
			(21.4[a])	(165[a])

[a] Measured in MeOH. [b] For table/entry 1/7 no reliable results could be obtained, as described in the text.

curve M_w (GPC) was calculated from the experimental elution curves and compared to M_w (LS). Whereas at intermediate retention times good agreement was observed, significant deviations were found at both very small and very large retention volumes. Such deviations are typical when calibration data are missing at the low or high molar mass end of the elution curves, because extrapolated calibration curves, in contrast to interpolated curves, are not reliable, particularly when close to the exclusion limits. "Artificial" data points—one at high and one at low retention time—were therefore added until the resulting calibration curve yielded good agreement for all values of M_w (GPC) and M_w (LS), except for the highest molar mass, as shown in Table 3. For comparison, the **PG1** and the classical, standard PMMA calibration curves are shown in Figure 2.

The retention time of the samples of highest molar mass is so close to the upper size-exclusion limit that the GPC columns utilized are not suitable for reliably providing the molar masses and molar mass distributions. For instance, Zimm plot analysis of sample 7, Table 1 yields a radius of gyration on the order of 200 nm (see below and Figure 5). For such large particles anomalous elution might yield irregular elution curves, as was demonstrated for similar samples

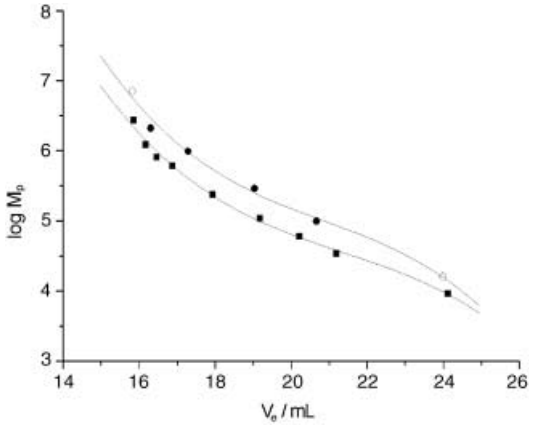


Figure 2. Calibration curves for **PG1** based on light scattering (●) and a PMMA standard (■). The open circles at low and high elution volumes represent artifical points for stabilizing the fit for the calibration curve.

by means of a light-scattering detector.[10] Very large molecules which should elute at the upper exclusion limit are retarded to larger elution volumes by an as-yet unknown elution mechanism. This would explain why the largest molar masses determined by light scattering are always much larger than those obtained by GPC. Another explanation could be that the highest molar masses form a significant fraction of aggregates which either fall apart during the GPC experiment or remain on the columns. However, this possibility is less likely, because the LS results for such samples were quite reproducible and did not show the typical signature of aggregates, that is, large fluctuations in count rate and loss of concentration by filtration.

Note that the LS calibration curve yields correct molar masses and molar mass distributions only for the **PG1** samples. When applied to higher generation polymers the molar masses are most probably smaller than the true ones. Since the effect of the mass of the larger repeat unit (r.u.) will be counterbalanced somewhat by an increase in chain stiffness (see below), the true molar masses are difficult to estimate. Unfortunately, all light-scattering investigations on **PG2**, **PG3**, and **PG4** in solvents such as MeOH, DMF, and THF failed so far, because of irreproducible results caused by the tendency of such polymers to form aggregates. To solve this problem a better solvent is needed.

The following conclusions can be drawn for the data of Table 1:

1) All yields of polymers are high (>75%), except for monomer **10** (entry 14).
2) For **PG1** (entries 1–7) the DMF data referenced to PMMA were compared with those calibrated by LS. The latter are consistently higher by a factor 2.4 than those obtained by PMMA calibration. Normalizing to the same degree of polymerization, that is, taking into account the significantly higher r.u. mass of **PG1** ($490\,g\,mol^{-1}$) compared to PMMA ($100\,g\,mol^{-1}$), the factor should be even larger. This, of course, requires the flexibility of the main chain and the solvent quality for PMMA and the dendronized polymer to be similar. The larger Kuhn statistical segment length of the dendronized polymers as compared to linear PMMA leads to a larger hydrodynamic volume. This increase, however, cannot compensate the opposite effect of the drastically increased mass per r.u. which, under the present experimental conditions, leads to the observed discrepancies in the GPC results.
3) It seems that TRP of monomer **5** in bulk produces increasing molar masses with increasing reaction time, which is unexpected for a radical polymerization. It is also noteworthy that truly high molar masses (entry 3) can be achieved under these conditions. Similarly to linear (unbranched) macromonomers,[11] the polymerization of dendronized macromonomers in benzene tends to give higher molar masses for higher concentrations (compare, e.g., entries 4 and 5 with 6 and 7 and entry 11 with entries 12 and 13). Finally, it is noteworthy that the third-generation macromonomer **10**, despite its considerable steric crowding near the polymerizable unit, furnishes polymer **PG3** with respectable apparent molar masses of $M_n = 820\,000$ and $M_w = 3\,400\,000$.
4) The apparent molar masses of **PG2** are lower than those of **PG1** (cf. entries 11–13 and 4–7). This effect is larger than the uncertainty in molar mass determination caused by the improper **PG1** calibration curve used for **PG2** (see above). For polymerizations with added initiator (entries 8–10) the PDI values become extremely broad once a certain initiator concentration is exceeded (compare entries 8 and 9 with entry 10). Polymerizations of **7** were carried out in saturated benzene solution ([M] = $0.30\,mol\,L^{-1}$). Experiments in bulk could not be performed because the melting point of this monomer is too high. The same holds for the higher generation monomers **10** and **12**. Because of the decreasing solubility of the monomers in benzene with increasing generation, polymerizations were performed in DMF (entries 12–15). Comparison of entry 11 (benzene) with entries 12 and 13 (DMF) shows that in the latter cases much higher apparent molar masses were achieved. It seems that the solubility aspect overcompensates the higher chain-transfer rate of DMF as compared to benzene. The maximum concentration for polymerization of G3 monomer **10** in DMF was $0.30\,mol\,L^{-1}$ (entry 14). Monomer **12** furnishes more or less oligomeric material in respectable yields. The GPC elution curves of representative samples of each generation (Figure 1a) show that the deviations from monomodality are largest for **PG4** and smallest for **PG1**.

Two main conclusions can be drawn from Table 2:

1) Considering the other monomers used so far for ATRP, those employed here are among those with the highest molar masses. Nevertheless, the molar masses of **PG1** and **PG2**, as well as the PDIs, are well within the range of those reported for ATRP, and the yields are high throughout.
2) As expected for a controlled radical polymerization, the dependency of molar mass on conversion (yield) is prac-

tically linear (entries 2–7 and Figure 3). The dependency of $\ln([M]_0/[M]_t)$ on polymerization time is also reasonably linear for conversions up to almost 80%, which are reached after 1 h (Figure 3). In contrast to many other ATRPs, monomer **5** polymerizes at a very high rate. Already after 10 min a conversion of at least 55% is reached.

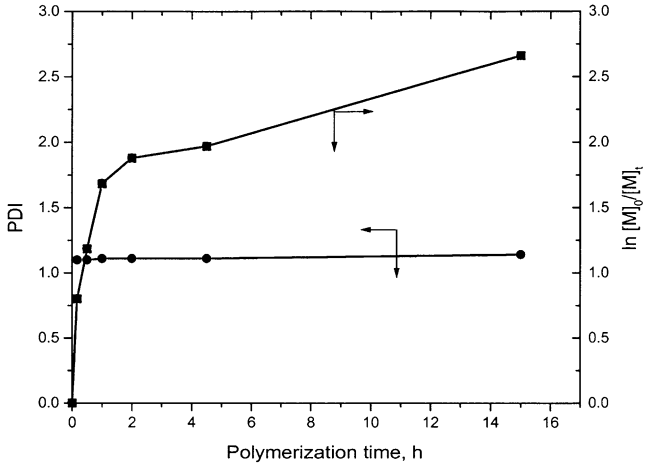


Figure 3. Kinetics (filled squares) and PDI dependence (filled circles) of ATRP of **5** on polymerization time. For polymerization conditions, see Table 2 (entries 2 and 7).

Static and dynamic light scattering: Static and dynamic light scattering was performed on five selected G1 samples; the results are summarized in Table 3. Figures 4 and 5 show the Zimm plots of **PG1** samples 1/1 and 1/7, respectively. Sample 1/1 shows a linear q^2 dependence of the reduced scattering intensity, that is, molar mass and radius of gyration could be reliably determined. Figure 4 is representative for all samples measured. Only for the highest molar mass sample could M_w and the square root of the mean square radius of gyration $R_{g,z}$ not be reliably determined, because the scattering envelopes were slightly curved and $R_{g,z}$ was too large to meet the condition $qR_{g,z}<1$. Utilizing the Kratky–Porod wormlike-chain model the Kuhn statistical

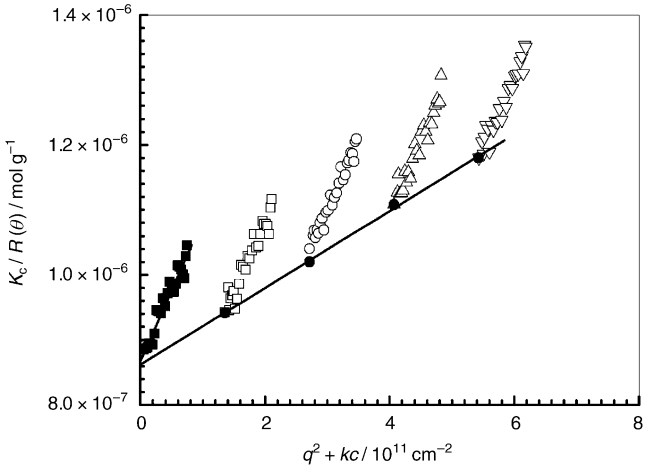


Figure 4. Zimm plot of **PG1** (Table 1, entry 1) in DMF.

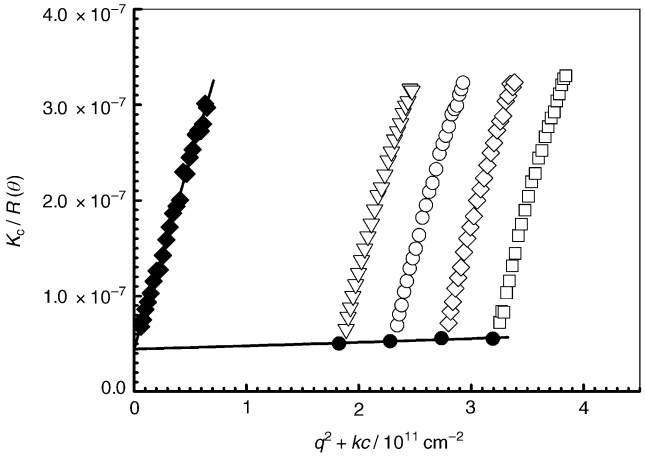


Figure 5. Zimm plot of **PG1** (Table 1, entry 7) in DMF.

segment length l_k can be estimated by Equation (1)[12,13],

$$R_{g,z}^2 = \frac{(m+2)l_k}{6y} - \frac{l_k^2}{4} + \frac{l_k^3}{4m(m+1)} + \frac{l_k^4}{8m(m+1)}\left(y^2 - \frac{y^{m+2}}{(y+2/l_k)^m}\right) \quad (1)$$

where $y=(m+1)/L_w$ and L_w is the weight-average contour length given by $L_w=P_w l$ (P_w is the weight-average degree of polymerization), l the contour length of a monomer unit, and m the Schulz–Zimm convolution parameter, which is related to the polydispersity by $M_w/M_n=1+m^{-1}$ The best fit of the $R_{g,z}$ data to Equation (1) is obtained with a Kuhn statistical segment length of $l_k=6$ nm (Table 4), which indicates a significant stiffening of the methacrylate main chain, most probably caused by the steric repulsion of the bulky side chains.

Table 4. Comparison of the experimental and calculated radii of gyration for some selected samples.[a]

Table	Entry	$10^{-6}M_w$ (LS) [g mol^{-1}]	$R_{g,z}$ [nm]	L_w [nm] [nm]	m	$R_{g,z}$ (calcd)
2	7	0.116	<10	59	4	7.9
2	8	0.287	13.3	146	5	12.2
1	1	1.14	26.7	580	1	29.4
1	2	2.3	44.6	1170	1	41.8

[a] For the calculated values according to Equation (1) the Kuhn statistical segment length of $l_k=6$ nm and the Zimm convolution parameter m as shown in the table were utilized.

Note that the above analysis is based on the assumption that excluded-volume effects are negligible. This is most probably justified because l_k does not increase with molar mass, which would artificially result for excluded-volume chains, and because of the poor solubility of the polymers. It is also assumed that the contour length of the chains is given by the fully stretched conformation, that is, 0.25 nm per monomer unit. As known for polymacromonomers with linear side chains[10,11b] this assumption may not be realistic

if the polymers adopt the shape of cylinders. In this case the length of the cylinder could be significantly smaller than the fully stretched main chain, that is, the main chain might adopt a locally coiled conformation. According to Equation (1) a smaller contour length L_w results in a larger Kuhn statistical segment length. Thus, the value of $l_k = 6$ nm given above represents the lower limit of chain stiffness, provided the excluded-volume effects do not have a significant influence.

Conclusion

Thermally induced radical polymerization can be successfully applied to the first- to fourth-generation macromonomers **5**, **7**, **10**, and **12**. It is superior to ATRP as far as high molar mass materials are concerned. Experimentally, TRP is simple since no addition of any reagent is required. The mere fact that these enormously sterically crowded monomers can polymerize without intentional addition of initiator mirrors a considerable and somewhat unexpected reactivity. ATRP can be performed with dendronized macromonomers up to G2, but reaction conditions could not be found which allowed these monomers to be used at initiator ratios greater than 300:1 (for **5**) and 100:1 (for **7**) and yet still furnish monomodal material. This limited the achievable molar masses in both cases to approximately 100000 g mol^{-1}.

Furthermore, the data in Table 1 show that it is essential for all monomers to use the most concentrated polymerization media possible to achieve high molar masses. Insufficient concentration makes polymerization to very high molar masses impossible and may give the false impression that it is infeasible.

The true molar masses determined by light scattering were significantly higher than those obtained by GPC with a linear PMMA calibration curve. For the presently investigated polymers the polydispersity determined by calibration curves utilizing absolute light-scattering molar masses and linear PMMA standards were comparable. The Kuhn statistical segment length of the PG1 generation was estimated to a minimum value of $l_k = 6$ nm by wormlike-chain analysis of the radius of gyration.

Experimental Section

General procedures: Compounds **1**,[14] **3a**,[8] **3b**,[15] and **8a**[8] were synthesized according to literature methods. Other reagents were purchased from Aldrich or Fluka. Methacryloyl chloride (MAC) was freshly distilled before use. CuBr (95%) was purified according to a literature procedure.[16] THF was refluxed over LAH, and 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. For determination of the macromonomer concentration the volume change associated with a large mass dissolved in a small volume of solute was taken into account. Silica gel 60M (Macherey-Nagel, 0.04–0.063 mm/230–400 mesh) was used as the stationary phase for column chromatography. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM 270 and AC 500 spectrometers at room temperature. Mass spectrometry was carried out on a Varian MAT 711 spectrometer. The FAB experiments were carried out with 3-nitrobenzyl alcohol (MNBA)/CH_2Cl_2, for the MALDI-TOF experiments THA was used as matrix. Elemental analysis was performed on a Perkin-Elmer EA 240. The samples were dried rigorously under vacuum prior to analysis to remove strongly adhering solvent molecules. Gel permeation chromatography (GPC) measurements were carried out using Waters ultra styragel columns ($10^4+10^3+10^2$ nm) with RI (refractive index) and UV (268 nm) detectors (poly(methyl methacrylate) standards, DMF + 1 g L^{-1} LiBr as eluent, room temperature). To exclude that the high molar masses observed are influenced by concentration effects it was verified for some selected samples (curves 1 and 4 in Figures 1a and b, respectively) that the elution curves do not change when the injection concentration is changed from 10 g L^{-1} to 1 g L^{-1}. Measurements were typically performed in a concentration range of 2–3 g L^{-1}. Static light-scattering measurements were performed with an ALV-SP86 goniometer, an Uniphase HeNe laser (25 mW output power at 632.8 nm wavelength) and an ALV/High QE APD avalanche diode fiberoptic detection system. The dilute polymer solutions in DMF or MeOH (typically 4–5 concentrations in the range $0.1 \le c \le 2$ g L^{-1}) were measured from 30 to 150° in steps of 5°. Prior to measurement the solutions were filtered through 0.2 μm pore Dimex filters (Millipore LG). The refractive index increment was measured by a home-built Michelson interferometer, as described elsewhere,[17] and determined to $dn/dc = 0.0802$ cm^3 g^{-1} in DMF and $dn/dc = 0.176$ cm^3 g^{-1} in MeOH. **PG1** samples showed a slight tendency to aggregate, which could be minimized by selection of proper solvents (DMF and MeOH) and by careful filtration. Control measurements in MeOH gave identical results within experimental error of ±10% for M_w and $R_{g,z}$. LS investigations on **PG2** samples were not successful, that is, not reproducible in DMF, MeOH, $CHCl_3$, and THF, because of a significant tendency to aggregate. All measurements resulted in curved scattering envelopes and in an unacceptably large variance between different concentrations.

3,5-Bis-[3-(*tert*-butyloxycarbonylamino)propyl]benzyl alcohol (4a): A solution of **3a** (30 g, 64.6 mmol) in THF (200 mL) was added dropwise to a slurry of $LiAlH_4$ (3.68 g, 97.0 mmol) in THF (600 mL) over 1 h at 0°C. The reaction mixture was warmed to room temperature, stirred for 16 h, then quenched by dropwise addition of water (30 mL), 15% NaOH (40 mL), and water (30 mL). The resulting precipitate was filtered, and THF evaporated off. Chromatographic separation (hexane/ethyl acetate 3/1) gave **4a** as a colorless oil (25.4 g, 93%). ^{1}H NMR ($CDCl_3$): $\delta = 1.39$ (s, 18H; CH_3), 1.73 (m, 4H; CH_2), 2.54 (m, 4H; CH_2Ph), 2.72 (br, 1H; OH), 3.05 (m, 4H; CH_2NH), 4.56 (s, 2H; OCH_2Ph), 4.73 (br, 2H; NH), 6.85 (s, 1H; Ph), 6.94 ppm (s, 2H; Ph); ^{13}C NMR ($CDCl_3$): $\delta = 28.33$, 31.51, 32.80, 39.96, 64.96, 79.04, 124.60, 127.57, 141.34, 141.77, 156.00 ppm; FABMS (3 kV): m/z (%): 423 (4.30) $[M+H]^+$. elemental analysis (%) calcd for $C_{23}H_{38}N_2O_5$ (422.56): C 65.37, H 9.06, N 6.63; found: C 65.19, H 9.02, N 6.41.

3,5-Bis-(3-aminopropyl)benzyl alcohol·2HCl (4b): 25% HCl (18.14 g, 124.2 mmol) was added to a solution of **4a** (10.5 g, 24.85 mmol) in THF (300 mL) at 0°C, and the mixture stirred for 4 h. Evaporation of the solvent at room temperature yielded **4b** as a colorless semisolid product (7.04 g, 96%). ^{1}H NMR (D_2O): $\delta = 1.98$ (m, 4H; CH_2), 2.71 (m, 4H; CH_2Ph), 3.00 (m, 4H; CH_2NH), 4.59 (s, 2H; OCH_2Ph), 7.13 ppm (s, 3H; Ph); ^{13}C NMR (D_2O): $\delta = 30.85$, 34.12, 41.51, 66.12, 127.71, 130.27, 143.40, 144.08 ppm; FABMS (3 kV): m/z (%): 223 (5.51) $[M-2HCl+H]^+$; elemental analysis (%) calcd for $C_{13}H_{24}Cl_2N_2O$ (295.25): C 52.88, H 8.19, N 9.49; found: C 52.68, H 8.15, N 9.27.

3,5-Bis-(3-*tert*-butoxycarbonylaminopropyl)benzyl methacrylate (5): A solution of MAC (7.42 g, 71.0 mmol) in THF (100 mL) was added dropwise to a mixture of **4a** (20 g, 47.3 mmol), triethylamine (TEA; 14.4 g, 142.3 mmol), and dimethylaminopyridine (DMAP; 0.2 g) in dry THF (200 mL) at 0°C over 30 min. The mixture was stirred for 12 h at room temperature, then washed with aqueous $NaHCO_3$ and brine. The organic phase was dried with magnesium sulfate, and the solvents were evaporated under vacuum at RT. Chromatographic separation (silica gel, ethyl acetate/hexane 1/3), performed twice, yielded **5** as a colorless solid (21.9 g, 94%). M.p. 85°C. ^{1}H NMR ($CDCl_3$): $\delta = 1.41$ (s, 18H; CH_3), 1.77 (m, 4H; CH_2), 1.94 (t, 3H; CH_3), 2.59 (m, 4H; CH_2Ph), 3.12 (m, 4H; CH_2NH), 4.60 (br, 2H; NH), 5.10 (s, 2H; OCH_2Ph), 5.56 (m, 1H; C=CH_2), 6.12 (m, 1H; C=CH_2), 6.93 (s, 1H; Ph), 6.97 ppm (s, 2H; Ph); ^{13}C NMR ($CDCl_3$): $\delta = 18.32$, 28.39, 31.62, 32.86, 40.09, 66.36, 78.67, 125.72, 128.33, 136.30, 142.02, 155.96, 165.00 ppm; FABMS (3 kV): m/z (%): 491

(1.58) $[M+H]^+$; elemental analysis (%) calcd for $C_{27}H_{42}N_2O_6$ (490.63): C 66.10, H 8.63, N 5.71; found: C 65.83, H 8.49, N 5.47.

3,5-[Bis(3-{3,5-bis[3-(*tert*-butyloxycarbonylamino)propyl]benzoyl}amino)-propyl]benzyl alcohol (6a): *N*-Hydroxybenzotriazole (9.16 g, 67.80 mmol) was added to a solution of acid **3b** (28.20 g, 64.60 mmol) in dry DCM (200 mL) at room temperature. After 10 min *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (13.62 g, 71.04 mmol) was added at −30 °C, and the reaction mixture was stirred until the hydrochloride was dissolved completely (ca. 3 h). Then a solution of TEA (16.32 g, 161.2 mmol) and **4b** (9.04 g, 30.62 mmol) in methanol/DCM (100 mL, 1/1) was added dropwise at −20 °C. The resulting mixture was warmed to room temperature, stirred for 14 h, and then washed with aqueous $NaHCO_3$ and brine. The organic layer was dried with magnesium sulfate, and the solvent removed in vacuo. Chromatographic separation (silica gel, ethyl acetate/hexane 2/1, 5/1) yielded **6a** as a colorless foam (21.0 g, 65 %). ^{1}H NMR ($CDCl_3$): δ = 1.39 (s, 36H; CH_3), 1.71 (m, 8H; CH_2), 1.89 (m, 4H; CH_2), 2.58 (m, 12H; CH_2Ph), 3.03 (m, 8H; CH_2NH), 3.36 (m, 4H; CH_2NH), 4.55 (s, 2H; OCH_2Ph), 4.81 (br, 4H; NH), 6.90 (s, 1H; Ph), 6.97 (s, 2H; Ph), 7.03 (s, 2H; Ph), 7.09 (br, 2H; NH), 7.35 ppm (s, 4H; Ph); ^{13}C NMR ($CDCl_3$): δ = 28.42, 30.79, 31.37, 32.51, 33.29, 39.64, 64.96, 79.19, 124.80, 127.63, 131.51, 134.83, 141.55, 141.81, 141.93, 156.13, 167.78 ppm; FABMS (3 kV): *m/z* (%): 1060 (0.12) $[M+H]^+$, 1082 (0.06) $[M+Na]^+$; elemental analysis (%) calcd for $C_{59}H_{90}N_6O_{11}$ (1059.38): C 66.89, H 8.56, N 7.93; found: C 66.53, H 8.41, N 7.79.

3,5-[Bis(3-{3,5-bis[3-amino propyl]benzoyl}amino)propyl]benzyl alcohol·4HCl (6b): 25 % HCl (1.42 g, 9.72 mmol) was added to a solution of **6a** (2.06 g, 1.94 mmol) in THF (150 mL) at 0 °C, and the mixture stirred for 4 h. Evaporation of the solvent at room temperature yielded **6b** as a colorless foam (1.51 g, 97 %). ^{1}H NMR (CD_3OD): δ = 1.94–2.05 (m, 12H; CH_2), 2.64 (m, 4H; CH_2Ph), 2.75 (m, 8H; CH_2Ph), 2.96 (m, 8H; CH_2NH), 3.40 (m, 4H; CH_2NH), 4.55 (s, 2H; CH_2O), 6.99 (s, 1H; Ph), 7.04(s, 2H; Ph), 7.36 (s, 2H; Ph), 7.56(s, 4H; Ph), 8.04 ppm (br, 2H; NH); ^{13}C NMR (CD_3OD): δ = 29.79, 31.81, 33.14, 34.19, 40.32, 41.04, 65.12, 125.78, 126.37, 128.53, 133.10, 135.38, 142.61, 143.09, 170.36 ppm; FABMS (3 KV), *m/z* (%): 659 (100) $[M-4HCl+H]^+$; elemental analysis (%) calcd for $C_{39}H_{62}C_{l4}N_6O_3$ (802.36): C 58.21, H 7.77, N 10.44; found: C 58.01, H 7.68, N 10.31.

3,5-[Bis-(3-{3,5-bis[3-(*tert*-butyloxycarbonylamino)propyl]benzoyl}amino)propyl]benzyl methacrylate (7): A solution of MAC (2.82 g, 26.98 mmol) in THF (100 mL) was added dropwise to a mixture of **6a** (19 g, 17.94 mmol), TEA (5.45 g, 53.8 mmol), and DMAP (0.2 g) in dry THF (200 mL) at 0 °C over 30 min. The mixture was stirred for 12 h at room temperature, then washed with aqueous $NaHCO_3$ and brine, and dried with magnesium sulfate. After evaporation of the solvent under vacuum at room temperature, chromatographic separation (silica gel, ethyl acetate/hexane 2/1), performed twice, yielded **7** as a colorless foam (19.4 g, 96 %). M.p. 108 °C. ^{1}H NMR ($CDCl_3$): δ = 1.40 (s, 36H; CH_3), 1.73 (m, 8H; CH_2), 1.91 (m, 7H; CH_2+CH_3), 2.56 (m, 8H; CH_2Ph), 2.66 (m, 4H; CH_2Ph), 3.04 (m, 8H; CH_2NH), 3.42 (m, 4H; CH_2NH), 4.74 (br, 4H; NH), 5.07 (s, 2H; OCH_2Ph), 5.54 (m, 1H; C=CH_2), 6.10 (s, 1H; C=CH_2), 6.97 (br, 2H; NH), 7.00 (br, 3H; Ph), 7.04 (s, 2H; Ph), 7.38 ppm (s, 4H; Ph); ^{13}C NMR ($CDCl_3$): δ = 18.33, 28.40, 30.95, 31.32, 33.11, 39.55, 66.39, 79.15, 124.81, 125.88, 128.45, 131.53, 134.87, 141.75, 142.06, 156.08, 162.62, 167.80 ppm; FABMS (3 kV): *m/z* (%): 1128 (0.66) $[M+H]^+$, 1150 (0.25) $[M+Na]^+$; elemental analysis (%) calcd for $C_{63}H_{94}N_6O_{12}$ (1127.45): C 67.11, H 8.40, N 7.45; found: C 66.89, H 8.29, N 7.31.

3,5-Bis-{3-[3,5-bis(3-*tert*-butoxycarbonylamino-propyl)benzoylamino]propyl}benzoic acid 2,5-dioxopyrrolidin-1-yl ester (8b): *N*-hydroxysuccinimide (HOSu; 0.67 g, 5.82 mmol) was added at room temperature to a solution of **8a** (5.20 g, 4.85 mmol) in dry CH_2Cl_2 (300 mL). The mixture was stirred for 15 min, then dicyclohexylcarbodiimide (DCC; 1.25 g, 6.06 mmol) was added at −20 °C. The resulting mixture was warmed to room temperature and stirred overnight. After the precipitate was filtered off, chromatographic separation (silica gel, hexane/ethyl acetate 1/2) gave **8b** as a colorless foam (5.59 g, 98 %). ^{1}H NMR ($CDCl_3$): δ = 1.38 (s, 36H; CH_3), 1.70 (m, 8H; CH_2), 1.91 (m, 4H; CH_2), 2.53 (m, 8H; CH_2Ph), 2.66 (m, 4H; CH_2Ph), 2.86 (s, 4H; CH_2), 3.01 (m, 8H; CH_2NH), 3.38 (m, 4H; CH_2NH), 4.79 (br, 4H; NH), 7.02 (s, 2H; Ph), 7.23 (br, 2H; NH), 7.34 (s, 1H; Ph), 7.40 (s, 4H; Ph), 7.72 ppm (s, 2H; Ph); ^{13}C NMR ($CDCl_3$): δ = 25.47, 28.34, 30.75, 31.21, 32.33, 32.76, 39.30, 39.49, 79.03, 124.82, 125.13, 127.96, 131.52, 134.66, 135.46, 141.70, 142.70, 156.07, 161.91, 167.89, 169.28 ppm; FABMS (7 kV): *m/z* (%): 1171 (16.69) $[M+H]^+$; elemental analysis (%) calcd for $C_{63}H_{91}N_7O_{14}$ (1170.44): C 64.65, H 7.84, N 8.38; found: C 64.32, H 8.08, N 8.41.

3,5-Bis-{3-[3,5-bis(3-{3,5-bis-(3-*tert*-butoxycarbonylaminopropyl)benzoylamino}propyl)benzoylamino]propyl}benzyl alcohol (9): Compound **4b** (0.50 g, 1.69 mmol) and TEA (0.68 g, 6.77 mmol) in methanol (20 mL) were added dropwise to a solution of **8b** (4.17 g, 3.56 mmol) in CH_2Cl_2 (100 mL) over 15 min at −30 °C. The resulting mixture was warmed to room temperature and stirred overnight. After washing with $NaHCO_3$ and brine, the organic layer was dried with magnesium sulfate, and the solvent removed in vacuo. Chromatographic separation (silica gel, DCM/methanol 25/1) gave **9** as a colorless foam (3.60 g, 91 %). ^{1}H NMR ($CDCl_3$): δ = 1.38 (s, 72H; CH_3), 1.70 (m, 16H; CH_2), 1.85 (m, 12H; CH_2), 2.53 (m, 24H; CH_2Ph), 3.00 (m, 16H; CH_2NH), 3.31 (m, 12H; CH_2NH), 4.53 (s, 2H; CH_2O), 4.88 (br, 8H; NH), 6.98 (s, 3H; Ph), 7.03 (s, 6H; Ph), 7.32 (s, 4H; Ph), 7.41 (s, 8H; Ph), 7.48 ppm (br, 6H; NH); ^{13}C NMR ($CDCl_3$): δ = 28.57, 30.47, 31.23, 32.73, 32.84, 39.75, 39.79, 73.77, 79.06, 124.85, 130.42, 131.60, 134.42, 141.77, 145.81, 156.12, 161.70, 168.03 ppm; FABMS (3 kV): *m/z* (%): 2332 (4.71) $[M+H]^+$; elemental analysis (%) calcd for $C_{131}H_{194}N_{14}O_{23}$ (2331.44): C 67.44, H 8.38, N 8.41; found: C 67.19, H 8.29, N 8.35.

3,5-Bis-{3-[3,5-bis-(3-{3,5-bis-(3-*tert*-butoxycarbonylaminopropyl)benzoylamino}propyl)benzoylamino]propyl}benzyl methacrylate (10): MAC (0.18 g, 1.72 mmol) in THF (50 mL) was added dropwise to a solution of **9** (2.60 g, 1.11 mmol), DMAP (0.1 g), and TEA (0.45 g, 4.44 mmol) in THF (150 mL) over 15 min at 0 °C. The resulting mixture was stirred overnight. After washing with $NaHCO_3$ and brine, the organic layer was dried with magnesium sulfate, and the solvent removed in vacuo at room temperature. Chromatographic separation (silica gel, hexane/ethyl acetate 1/5) gave **10** as a colorless foam (2.25 g, 84 %). ^{1}H NMR ($CDCl_3$): δ = 1.34 (s, 72H; CH_3), 1.70 (m, 16H; CH_2), 1.81 (m, 12H; CH_2), 1.88 (s, 3H; CH_3), 2.52 (m, 24H; CH_2Ph), 2.62 (m, 4H; CH_2Ph), 3.01 (m, 16H; CH_2NH), 3.30 (m, 8H; CH_2NH), 3.39 (m, 4H; CH_2NH), 4.90 (br, 8H; NH), 5.02 (s, 2H; CH_2O), 5.52 (m, 1H; CH_2=), 6.07 (s, 1H; CH_2=), 6.97 (s, 2H; Ph), 7.02 (s, 5H; Ph), 7.32 (s, 6H; Ph), 7.40 ppm (s, 8H; Ph); ^{13}C NMR ($CDCl_3$): δ = 18.24, 28.37, 30.80, 31.27, 32.44, 32.81, 39.30, 39.60, 77.47, 124.86, 131.50, 134.45, 141.70, 156.15, 167.95 ppm; FABMS (7 kV): *m/z* (%): 2300 (56.66) $[M-Boc]^+$, 2401 (20.10) $[M+H]^+$; elemental analysis (%) calcd for $C_{135}H_{198}N_{14}O_{24}$ (2399.47): C 67.53, H 8.31, N 8.17; found: C 67.41, H 8.19, N 8.06.

3,5-Bis-{3-[3,5-bis(3-{3,5-bis-(3-[3,5-bis-(3-*tert*-butoxycarbonylamino propyl)benzoylamino]propyl)benzoylamino}propyl)benzoylamino]propyl}-benzyl alcohol (11): A mixture of **6b** (0.32 g, 0.40 mmol) and TEA (0.81 g, 8.00 mmol) in methanol (10 mL) was added dropwise to **8b** (2.34 g, 2.00 mmol) in CH_2Cl_2 (150 mL) at −30 °C over 10 min. The resulting mixture was warmed to RT and stirred overnight. After washing with $NaHCO_3$ and brine, the organic phase was dried over magnesium sulfate, and the solvent removed in vacuo. Chromatographic separation (silica gel, DCM/methanol 20/1) yielded **11** as a colorless foam (1.6 g, 82 %). ^{1}H NMR ($CDCl_3$): δ = 1.37 (s, 144H; CH_3), 1.69 (m, 32H; CH_2), 1.80 (br, 28H; CH_2), 2.51 (m, 56H; CH_2Ph), 2.63 (br, 4H; CH_2Ph), 3.00 (br, 32H; CH_2NH), 3.28 (br, 24H; CH_2NH), 4.50 (s, 2H; CH_2O), 4.98 (br, 16H; NH), 7.00 (s, 7H; Ph), 7.03 (s, 14H; Ph), 7.36 (s, 8H; Ph), 7.43 (s, 16H; Ph), 7.50 (br, 8H; NH), 7.68 ppm (br, 6H; NH); ^{13}C NMR ($CDCl_3$): δ = 28.38, 30.55, 31.27, 32.50, 32.75, 39.28, 39.67, 79.00, 124.90, 131.54, 131.62, 134.51, 141.74, 141.83, 156.19, 168.07, 168.27 ppm. MS (MALDI-TOF): *m/z* (%): 4903.9 (100 %) ca. $[M+Na]^+$; elemental analysis (%) calcd for $C_{275}H_{402}N_{30}O_{47}$ (4877.00): C 67.68, H 8.30, N 8.61; found: C 67.59, H 8.17, N 8.52.

3,5-Bis-{3-[3,5-bis-(3-{3,5-bis(3-[3,5-bis(3-*tert*-butoxycarbonylaminopropyl)benzoylamino]propyl)benzoylamino}propyl)benzoylamino]propyl}-benzyl methacrylate (12): MAC (33 mg, 0.31 mmol) in THF (20 mL) was added dropwise to a mixture of **11** (1.02 g, 0.21 mmol), DMAP (0.15 g), and TEA (84 mg, 0.84 mmol) in THF (150 mL) at 0 °C over 10 min, and the resulting mixture was stirred overnight. After washing with $NaHCO_3$ and brine, the organic phase was dried over magnesium sulfate. Chromatographic separation (silica gel, DCM/methanol 20/1) yielded **12** as a colorless foam (0.85 g, 82 %). ^{1}H NMR ($CDCl_3$): δ = 1.34 (s, 144H; CH_3), 1.65 (br, 32H; CH_2), 1.75–1.82 (br, 31H; CH_3+CH_2), 2.45 (br, 60H; CH_2Ph), 2.92 (br, 32H; CH_2NH), 3.23 (br, 28H; CH_2NH), 4.95 (s, 2H; CH_2O), 5.04 (br, 16H; NH), 5.54 (s, 1H; CH_2=), 6.02 (s, 1H; CH_2=), 6.88

(s, 7H; Ph), 6.98 (s, 14H; Ph), 7.32 (s, 8H; Ph), 7.39 (s, 16H; Ph), 7.54 (br, 8H; NH), 7.70 ppm (br, 6H; NH); ^{13}C NMR ($CDCl_3$): δ = 18.14, 28.26, 30.48, 31.14, 32.38, 32.64, 39.14, 39.53, 67.72, 78.79, 124.78, 125.57, 125.76, 131.45, 134.47, 134.61, 135.92, 141.61, 141.68, 141.91, 156.07, 167.11, 167.90, 168.08 ppm; MS (MALDI-TOF): *m*/*z* (%): 4972.9 (100%) ca. $[M+Na]^+$. Elemental analysis (%) calcd for $C_{279}H_{406}N_{30}O_{48}$ (4945.03): C, 67.72; H, 8.27; N, 8.49. Found: C, 67.59; H, 8.09; N, 8.35.

3,5-Bis-(3-*tert*-butoxycarbonylaminopropyl)benzyl 2-bromoisobutyrate (13): A solution of 2-bromoisobutyryl bromide (0.74 g, 3.22 mmol) in THF (40 mL) was added dropwise to a solution of **4a** (0.91 g, 2.15 mmol), TEA (0.65 g, 6.42 mmol), and 0.2 g of DMAP in THF (50 mL) over 15 min at 0°C. The mixture was warmed to room temperature and stirred for 12 h, washed with saturated aqueous $NaHCO_3$ and brine, and dried with magnesium sulfate. After evaporation of the solvent, chromatographic separation (silica gel, ethyl acetate/hexane 1/3) gave **8** as a colorless viscous oil (1.10 g, 90%), which solidified after some time. ^{1}H NMR ($CDCl_3$): δ = 1.42 (s, 18H; CH_3), 1.77 (m, 4H; CH_2), 1.93 (s, 6H; CH_3), 2.59 (m, 4H; CH_2Ph), 3.10 (m, 4H; CH_2NH), 4.59 (br, 2H; NH), 5.12 (s, 2H; OCH_2Ph), 6.94 (s, 1H; Ph), 6.98 ppm (s, 2H; Ph); ^{13}C NMR ($CDCl_3$): δ = 28.40, 30.76, 31.59, 32.84, 40.08, 67.49, 79.25, 125.49, 128.54, 135.62, 142.04, 155.95, 174.4 ppm; FABMS (3 kV): *m*/*z* (%): 571 (0.69) $[M+H]^+$; elemental analysis (%) calcd for $C_{27}H_{43}BrN_2O_6$ (571.54): C 56.74, H 7.58, N 4.90; found: C 56.45, H 7.44, N 4.76.

General procedure of TRP in bulk (A): The monomer and DCM were placed in a 100 mL flask. The flask was connected to a rotary evaporator and immersed in a water bath at 55°C. After complete removal of the solvent with stirring, the flask was kept rotating in the bath for a further 8 h. The polymer formed during that period was dissolved in DCM and purified by column chromatography (silica gel, DCM eluent).

General procedure of TRP in solvent (B): The monomer and the solvent were placed in a Schlenk tube, and the mixture stirred until it became homogeneous. The concentration of the monomer was kept around 75 wt%. The mixture was immediately degassed by several freeze–pump–thaw cycles, and then kept at 55°C for a predetermined time. After polymerization, the polymer was dissolved in DCM and purified by column chromatography (silica gel, DCM eluent).

General procedure of ATRP (C): The monomer, toluene, CuBr, and PMDETA were placed a Schlenk tube, and the resulting mixture stirred until it turned homogeneously green (for detailed conditions, see Table 2). The mixture was immediately degassed several times by freeze–pump–thaw cycles, then initiator **13** was added. As soon as the initiator was added, the system turned homogeneously blue-green, indicating the start of polymerization. The mixture was kept at 55°C for a predetermined time. After polymerization, the catalyst was removed by adsorption filtration through a short silica column, and the resulting polymer was purified on a silica column with DCM as eluent.

Poly{3,5-bis(3-*tert*-butoxycarbonylaminopropyl)benzyl methacrylate} (PG1; entry 3 in Table 1): According to procedure A, monomer **5** (4.0 g) and DCM (50 mL) were used. After chromatographic separation the polymer was lyophilized from dioxane to give **PG1** (3.4 g, 86%) as a colorless foam. ^{1}H NMR ($CDCl_3$): δ = 0.72 (br, 2H; CH_2), 0.93 (br, 3H; CH_3), 1.38 (br, 18H; CH_3), 1.70 (br, 2H; CH_2), 2.49 (br, 2H; CH_2Ph), 3.02 (br, 2H; CH_2NH), 4.79 (br, 2H; NH), 5.27 (br, 2H; CH_2O), 6.87 ppm (br, 3H; Ph); ^{13}C NMR ($CDCl_3$): δ = 28.54, 31.56, 32.87, 40.20, 78.78, 125.86, 128.34, 135.30, 142.15, 156.17 ppm; elemental analysis (%) calcd for $(C_{27}H_{42}N_2O_6)_n$ $(490.63)_n$: C 66.10, H 8.63, N 5.71; found: C 65.90, H 8.44, N 5.62.

Poly{3,5-bis-(3-*tert*-butoxycarbonylaminopropyl)benzyl methacrylate} (PG1; entry 6 in Table 2): According to procedure C, CuBr (1.94 mg), PMDETA (7.07 mg), **13** (7.77 mg), **5** (2.0 g), and toluene (1.2 mL) were used. After chromatographic separation the polymer was lyophilized from dioxane to yield **PG1** (1.72 g, 86%) as a colorless foam. ^{1}H NMR ($CDCl_3$): δ = 0.72 (br, 2H; CH_2), 0.93 (br, 3H; CH_3), 1.38 (br, 18H; CH_3), 1.70 (br, 2H; CH_2), 2.49 (br, 2H; CH_2Ph), 3.02 (br, 2H; CH_2NH), 4.79 (br, 2H; NH), 5.27 (br, 2H; CH_2O), 6.87 ppm (br, 3H; Ph); ^{13}C NMR ($CDCl_3$): δ = 28.54, 31.56, 32.87, 40.20, 78.78, 125.86, 128.34, 135.30, 142.15, 156.17 ppm; elemental analysis (%) calcd for $(C_{27}H_{42}N_2O_6)_n$ $(490.63)_n$: C 66.10, H 8.63, N 5.71; found: C 66.40, H 8.41, N 5.67.

Poly{3,5-[bis(3-{3,5-bis[3-(*tert*-butyloxycarbonylamino)propyl]benzoyl}-amino)propyl]benzyl methacrylate} (PG2; entry 12 in Table 2): According to procedure C, CuBr (0.97 mg), PMDETA (3.54 mg), **13** (5.07 mg), **7** (2.0 g), and DMF (1.0 mL) were used**.** After chromatographic separation, the polymer was lyophilized from dioxane to give **PG2** (1.7 g, 85%) as a colorless foam. ^{1}H NMR ($CDCl_3$): δ = 0.65 (br, 2H; CH_2), 0.78 (br, 3H; CH_3), 1.30 (br, 36H; CH_3), 1.59 (br, 8H; CH_2), 1.70 (br, 4H; CH_2), 2.37 (br, 12H; CH_2Ph), 2.88 (br, 8H; CH_2NH), 3.20 (br, 4H; CH_2NH), 4.65 (br, 2H; CH_2O), 5.30 (br, 4H; NH), 6.82 (br, 3H; Ph), 6.94 (br, 2H; Ph), 7.43 ppm (br, 4H; Ph); ^{13}C NMR ($CDCl_3$): δ = 18.98, 28.38, 31.18, 32.49, 39.68, 41.17, 44.99, 78.66, 124.97, 128.11, 131.48, 134.56, 141.74, 156.18, 167.99, 176.98 ppm; elemental analysis (%) calcd for $(C_{63}H_{94}N_6O_{12})_n$ $(1127.45)_n$: C 67.11, H 8.40. N 7.45; found: C 66.86, H 8.23, N 7.39.

Poly(3,5-bis-{3-[3,5-bis-(3-{3,5-bis(3-*tert*-butoxycarbonylamino-propyl)-benzoylamino}propyl)benzoylamino]propyl}benzyl methacrylate) (PG3, entry 14 in Table 1): According to procedure B, monomer **10** (0.60 g), and DMF (0.30 mL) were used. After chromatographic separation the polymer was lyophilized from dioxane to yield **PG3** (0.30 g, 50%) as a colorless foam. ^{1}H NMR ($CDCl_3$): δ = 0.66 (br, 3H; CH_3), 0.80 (br, 2H; CH_2), 1.27 (br, 72H; CH_3), 1.58 (br, 28H; CH_2), 2.39 (br, 28H; CH_2Ph), 2.90–3.18 (br, 28H; CH_2NH), 5.17 (br, 10H; CH_2O + NH), 6.92 (br, 10H; Ph), 7.38 (br, 11H; Ph), 7.76 ppm (br, 6H; NH); ^{13}C NMR ($CDCl_3$): δ = 28.50, 31.31, 32.68, 39.97, 78.79, 125.04, 131.44, 134.82, 141.92, 156.30, 168.08 ppm; elemental analysis (%) calcd for $(C_{135}H_{198}N_{14}O_{24})_n$ $(2401.10)_n$: C 67.53, H 8.31, N 8.17; found: C 67.41, H 8.32, N 8.34.

Poly(3,5-bis{3-[3,5-bis(3-{3,5-bis(3-[3,5-bis(3-*tert*-butoxycarbonylamino-propyl)benzoylamino]propyl)benzoylamino}propyl)benzoylamino]propyl}benzyl methacrylate) (PG4; entry 15 in Table 1): According to procedure B, monomer **12** (0.50 g) and DMF (0.25 mL) were used. After chromatographic separation the polymer was lyophilized from dioxane to yield **PG4** (0.44 g, 88%) as a colorless foam. ^{1}H NMR ($CDCl_3$): δ = 0.72 (br, 3H; CH_3), 0.85 (br, 2H; CH_2), 1.30 (br, 144H; CH_3), 1.66 (br, 60H; CH_2), 2.42 (br, 60H; CH_2Ph), 2.94 (br, 32H; CH_2NH), 3.21 (br, 28H; CH_2NH), 4.96 (br, 2H; CH_2O), 5.28 (br, 16H; NH), 6.93 (br, 16H; Ph), 7.45 (br, 29H; Ph), 7.84–8.20 ppm (br, 14H; NH); ^{13}C NMR ($CDCl_3$): δ = 28.37, 30.58, 31.23, 32.52, 39.70, 78.77, 124.94, 131.52, 134.52, 141.79, 156.23, 168.04 ppm; elemental analysis (%) for $(C_{279}H_{406}N_{30}O_{48})_n$ $(4945.03)_n$: C 67.72, H 8.27, N 8.49; found: C 67.80, H 8.13, N 8.41.

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