

Homologous Series of Dendronized Polymethacrylates with a Methyleneoxycarbonyl Spacer between the Backbone and Dendritic Side Chain: Synthesis, Characterization, and Some Bulk Properties

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Abstract: First through fourth generation (G1–G4) dendronized macromonomers, **3**, **5**, **7**, and **9**, with a methyleneoxycarbonyl spacer between the polymerizable group and dendritic side chain (dendron) were synthesized, and their polymerization behavior to the corresponding dendronized polymers **PG1s**, **PG2s**, **PG3s**, and **PG4s**, respectively, was investigated by heating the monomers to 55 °C without intentional addition of initiator. This self-induced polymerization is referred to as thermally induced radical polymerization (TRP). The molar masses of **PG1s**–**PG4s** were determined by gel permeation chromatography in DMF calibrated to a recently developed G1 dendronized polymer standard (**PG1**). A comparison of this homologous series' polymerization results with those of an already existing one, which differed only by the lack of this spacer (referred to as **PG1**–**PG4**), was made to contribute to the issue of whether short spacers have an effect on polymerization. Several representatives of both series were also used in the first systematic and generation-dependent investigation of these unusual comb polymers' bulk properties. Both structure and dynamics were investigated by DSC, X-ray diffraction, and dynamic mechanical measurements.

1. Introduction

Up to now, most macromonomers applied in the synthesis of dendronized polymers¹ carry a spacer between the polymerizable group and the appendent dendron. Those without are sometimes reported to only give oligomeric product.² It was reasoned that having a distance between these units may be essential for the obtainment of high molar mass materials because a spacer could help decrease steric congestion around the polymerizable unit. On the other hand, Percec reported on a considerable rate enhancement of the radical polymerization of styrenic and acrylic dendronized macromonomers which did not carry a spacer but were preorganized prior to polymerization so that the polymerizable units were kept at a short distance from one another by the packing behavior of their adjacent mesogenic dendrons.³ Besides the question of whether preorganization plays a role, there are many other factors which

render it difficult to decide whether there is a spacer effect. For example, such simple things as the monomers' achievable degree of purity as well as their melting points, mobilities in highly concentrated solutions or in the melt, and solubilities in an unpredictable way depend on the presence or absence of a spacer and may well delude one to draw wrong conclusions from experimental results. Especially, the latter two aspects may become critical because polymerizations of macromonomers are usually done in highly concentrated solution or even in bulk.⁴ If the monomer with spacer happens to give more highly concentrated solutions, it may give higher molar mass product just for that reason. We therefore set out to look more deeply and systematically into this matter. Recently, a series of polymethacrylate-based first through fourth generation (G1–G4) dendronized polymers (**PG1**–**PG4**) were prepared.⁵ High molar mass material was obtained up to the third generation (**PG3**), and even G4 monomers gave high oligomers (**PG4**) in high yields. We here report the synthesis and polymerization of the exact same series of monomers with the only difference being a methyleneoxycarbonyl spacer between the polymerizable group (methacrylate) and the dendritic substituent. The three factors of yield, approximate polymerization time, and molar

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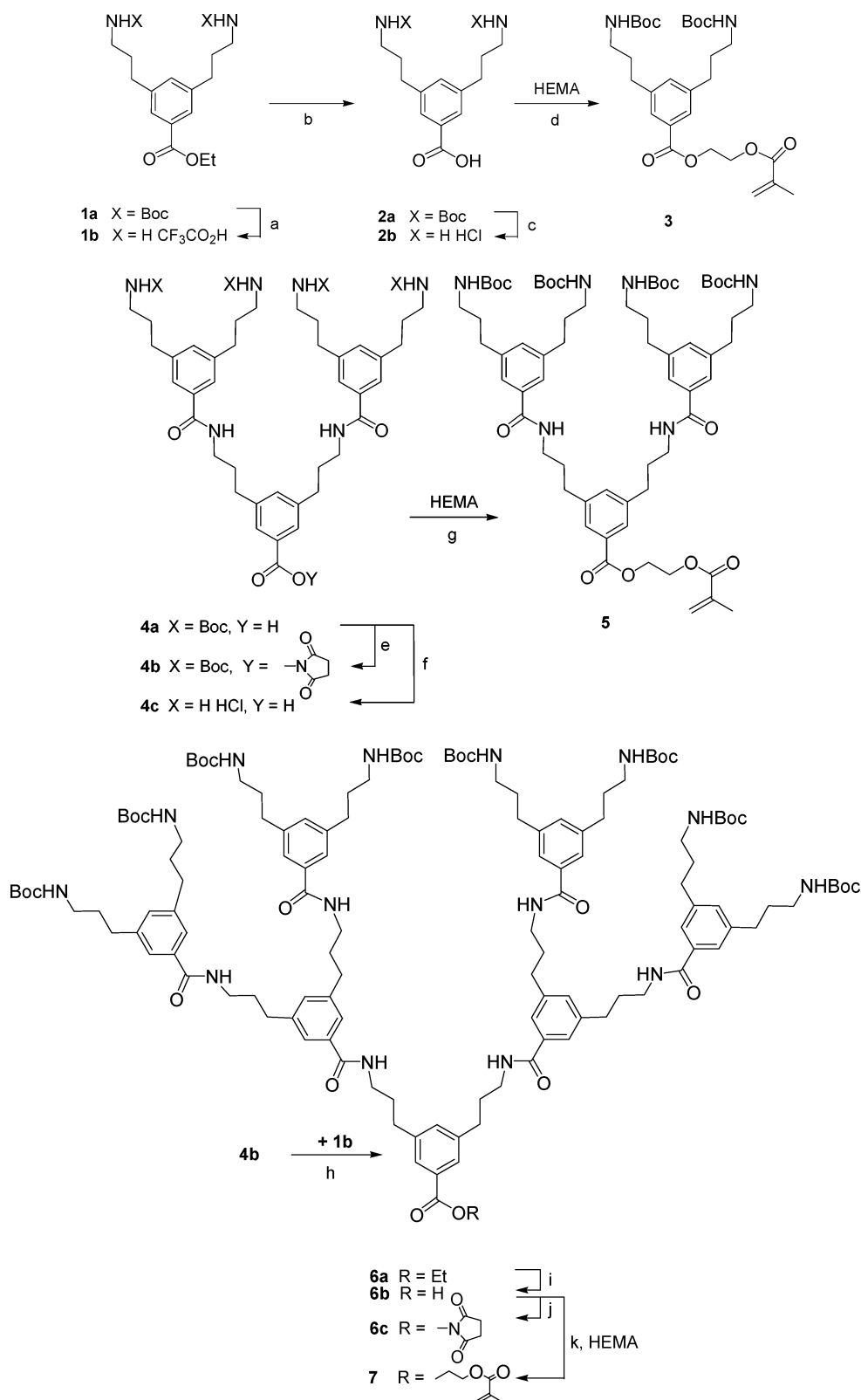
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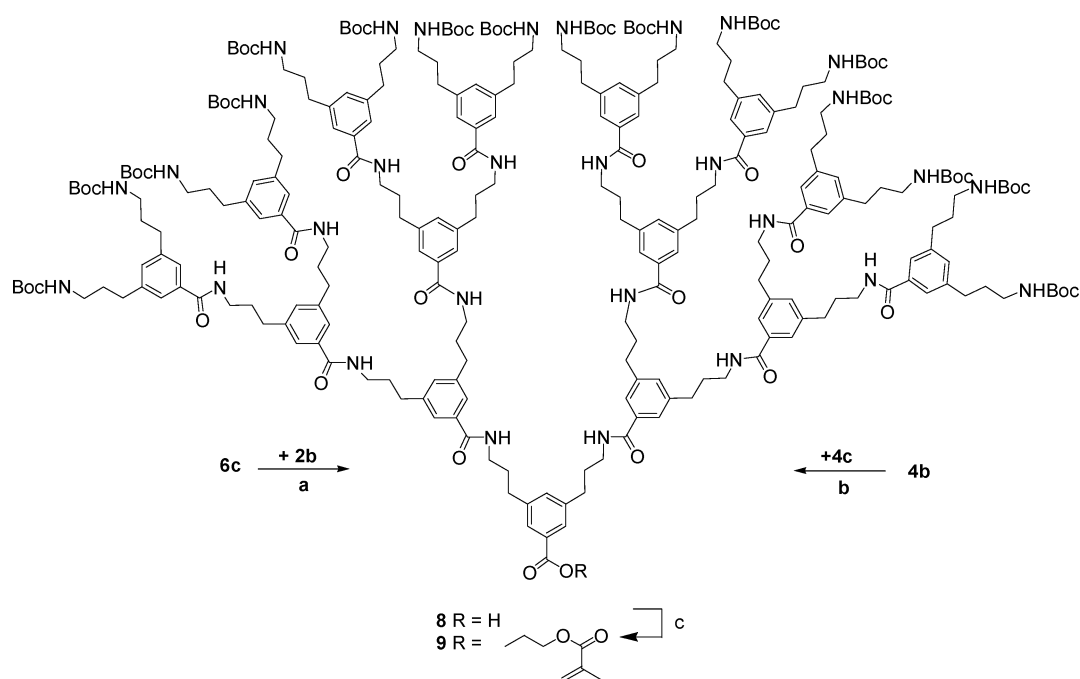
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Scheme 1^a

^a Reagents and conditions: (a) **1a**, TFA, 0 °C, 12 h (95%); (b) **1a**, KOH, 50 °C, 6 h (91%); (c) **2a**, 25% HCl, THF, 0 °C, 4 h (98%); (d) **2a**, HEMA, DMAP, DCC, DCM, room temperature, 12 h (98%); (e) **4a**, DCC, HOSu, DCM, 12 h, -20 °C (98%); (f) **4a**, 25% HCl, THF, 0 °C, 4 h (98%); (g) **4a**, DCC, DMAP, HEMA, DCM, room temperature, 12 h (92%); (h) **1b**, **4b**, TEA, DCM, -30 °C, 12 h (87%); (i) **6a**, KOH, MeOH, THF, 12 h, 50 °C (86%); (j) **6b**, DCC, HOSu, DCM, -20 °C (92%); (k) **6b**, HEMA, DMAP, DCC, DCM, room temperature, 12 h (96%).

mass of the obtained polymers **PG1s–PG4s** were used for comparison with the above series and to address the spacer issue (the small *s* indicates the existence of the spacer). Having both

of these homologous series in hand, we had another important goal of substantially furthering the scarce knowledge on the bulk properties of these unusual comb polymers by performing

Scheme 2^a

^a Reagents and conditions: (a) **2b**, **6c**, TEA, DCM, MeOH, $-20\text{ }^\circ\text{C}$, 12 h (75%); (b) **4b**, **4c**, TEA, MeOH, DCM, $-30\text{ }^\circ\text{C}$, 12 h (78%); (c) **8**, HEMA, DCC, DMAP, DCM, room temperature, 12 h (92%).

a systematic, generation-dependent investigation by DSC, X-ray diffraction, and dynamic mechanical analysis. As a side effect, this should also provide insight into whether the short spacer has an influence on bulk properties.

2. Results and Discussion

Macromonomer Synthesis. The syntheses of macromonomers **3**, **5**, **7**, and **9** are shown in Schemes 1 and 2. For the first two monomers **3** and **5**, they are closely related to known work^{5,6} and will therefore not be further discussed in detail here. For the couplings of the dendrons **2a** and **4a** to the polymerizable unit, hydroxyethyl methacrylate (HEMA), the DCC method was applied.⁷ The G3 dendron **6a** was obtained from G2 active ester **4b** and the G1 branching unit **1b** in a yield of 78% despite the relatively low excess of **4b** (1.05 equiv per amine). This way only two coupling steps were required and the achievable yield was expected to be higher than in the opposite case (not shown) in which a G1 fragment is attached to a G2 dendron with its four amine coupling sites. The saponification of **6a** required a longer amount of time than in the related lower generation cases. Coupling of G3 acid **6b** to HEMA afforded the G3 macromonomer **7**. The synthesis of the G4 dendron **8** was attempted from different sides. First, the corresponding succinidyl active ester **6c** was coupled to branching unit **1b**. This gave a G4 dendron with an ester group at its focal point (not shown). Its saponification could not be achieved with standard methods because of the relatively narrow range of conditions applicable. Basically, starting material was recovered. Next, the reaction between the active ester dendron **6c** and the branching unit **2b** was tried. Branching unit **2b**, in contrast to **1b**, has a carboxylic acid at its focal point. Although the coupling to **8** worked nicely, the

synthetic effort involved in **6c** was considered too high. Finally, the synthesis of **8** was done through the coupling of the two G2 building blocks **4b** and **4c**. Dendron **8** was obtained in a yield of 80%. The corresponding monomer **9** was obtained by esterification with HEMA as described above. All intermediate compounds and the four monomers were characterized by their fully assigned ¹H, ¹³C NMR spectra, mass spectra (FAB or MALDI-TOF), and correct data from combustion analysis.

Thermally Induced Polymerization. Highly concentrated solutions of the monomers **3**, **5**, **7**, and **9** were heated to $55\text{ }^\circ\text{C}$ without any initiator added, and the resulting polymers **PG1s**–**PG4s**, respectively, were isolated after predetermined times by simple precipitation. Details on these polymerizations are given in Table 1 and can also be found in the Supporting Information. The polymers were characterized by their ¹H and ¹³C NMR spectra and the correct data from combustion analysis. Upon increases in both generation and molar mass, the NMR signals became broader and broader, and, thus, the assignment was less reliable. The molar masses of all polymers were determined by GPC in DMF using a recently developed **PG1** standard.⁵ Representative results are shown in Table 1. Each entry has been reproduced at least three times for **PG1** and **PG2** and two times for **PG3**. The polymerization to **PG4** has been carried out only once.

A comparison of the dendronized polymers' molar masses achieved in both homologous series, **PG1**–**PG4** and **PG1s**–**PG4s**, can only be done on a qualitative level for reasons which include the possible presence of unknown trace impurities in some of the samples and the fact that for each monomer pair of the same generation, but with and without oxyethylene spacer, respectively, the concentrations of the saturated polymerization media varied up to a few percent. For experimental simplicity, all polymerizations were carried out in the same amount of solvent using the same quantity of macromonomer. This concentration

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Table 1. Conditions and Results for the Radical Polymerization of Monomers **3**, **5**, **7**, and **9** To Give Polymers **PG1s–PG4s**, Respectively (Entries 1–7), and for Comparison Purposes the Corresponding Information for **PG1–PG4** (Entries 8–11)^a

entry	monomers	polymerization conditions ^b		yield %	GPC (PG1) ^c				
		[M], mol/L	time, h		$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n	DP _n	DP _w
1	3	1.22	16	89	162.5	560.6	3.45	2962	10 219
2	3	1.22	72	88	149.2	608.7	4.08	2719	11 094
3	5	0.51	14	52	84.8	351.9	4.15	715	2967
4	5	0.51	20	57	77.0	365.0	4.74	650	3081
5	7	0.25	16	48	40.8	119.5	2.93	166	486
6	7	0.25	38	50	43.1	123.3	2.86	175	500
7 ^d	9	0.14	48	12	11.7	16.3	1.39	23	32
8 ^e	G1	1.36	5.5	78	150.8	642.4	4.26	3074	12 980
9 ^e	G2	0.60	48	86	73.0	247.5	3.39	647	2193
10 ^e	G3	0.30	30	50	81.9	325.1	3.97	341	1354
11 ^e	G4	0.14	48	88	15.0	24.2	1.61	30	48

^a **PG1s–PG4s** and **PG1–PG4** are referred to as dendronized polymethacrylate with and without a methyleneoxycarbonyl spacer between the polymerizable group and dendritic side chain, respectively. ^b Carried out at 55 °C in benzene. ^c GPC in DMF at 30 °C calibrated with light scattering data obtained for **PG1**. ^d DMF as polymerization solvent. ^e Data from Table 1 of ref 5.

difference may have had some effect on the achieved molar mass. The comparison is based on entries 1–7 and 8–11 of Table 1, respectively, the latter of which had already been published.⁵ It can be seen that both of the molar mass ranges achieved for the different generations vary only by approximately $\pm 10\%$ except for the **G3** case. Here, **PG3s** has by a factor of 2 lower molar mass than **PG3** which is actually in contrast to what one intuitively might have expected. Also, the trend to shorter chains with increasing dendron generation is the same. Finally, as judged from the total polymerization times, there also does not seem to be much difference in polymerization rate for comparable generations, although a thorough kinetic study would be required to substantiate this point. Thus, considering the large amount of samples of both series involved in this study, it can be concluded with some confidence that there is no significant spacer effect for all four macromonomer pairs. Even for the **G4** monomers, where steric hindrance supposedly plays the most important role, basically the same results were obtained (except for the yields).

Comment on Spacers. There seems to be no common understanding as to what a spacer is in polymer synthesis. Most vinyl polymerizable units require additional substituents to attain sufficient reactivity to polymerize. For acrylates and styrenes, for example, this would be the ester and phenyl group, respectively. Because these substituents are a prerequisite for the polymerization, they are not normally referred to as spacers, although, besides their activating nature, they certainly contribute to keep the substituents at the ester or phenyl groups apart from the polymerizing vinyl. As a result, an acrylate monomer with a methyleneoxy “spacer” keeps a substituent bound to the spacer not much further apart from the polymerizable unit as a styrene to which this very same substituent is bound directly in the *para*-position, even though the use of the term spacer in the former implies this. Although several factors influence the propensity of a given polymerizable unit to polymerize in differently substituted monomers of the same kind (e.g., **G1–G4** dendronized methacrylates), it may be helpful to more rigorously define the spacer as the entire fragment in its stretched conformation which connects the vinyl carbon atom of the polymerizable unit with an arbitrarily chosen part of the substituent in question (e.g., a dendron). This way, the ester group of MMA represents a spacer of approximately 2.5 Å length, and the phenyl group in styrenes (if the substituent is

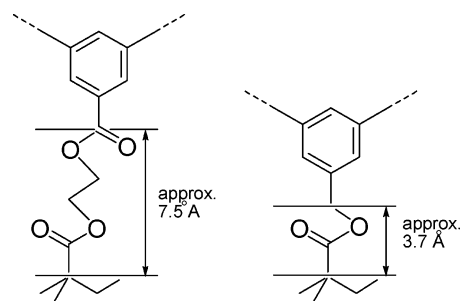


Figure 1. More adequate than commonly defined spacers in the “spacerless” series of dendronized polymers **PG1–PG4** and in the series with a so-called methyleneoxycarbonyl spacer **PG1s–PG4s**.

connected to it in the *para*-position) represents a length of 3.7 Å. The “spacerless” **PG1–PG4** series would then, in fact, have a spacer of approximately 3.7 Å, and the **PG1s–PG4s** series would have a spacer of 7.5 Å (Figure 1).

Polymer Characterization. Differential Scanning Calorimetry (DSC). All polymers were at room temperature in an amorphous glassy state. When heated, they underwent softening related to the glass transition (T_g). Figure 2 shows the second heating DSC traces for both **PG1–PG4** and **PG1s–PG4s** series with clearly visible enthalpy steps in all samples. The T_g values were determined from the middle point in these steps and are listed in Table 2. In both series, they increase with dendron generation up to the third generation but become lower again for the fourth generation.

This increase by approximately 10 °C is remarkable and means that the segmental mobility for a temperature slightly above the highest T_g could for different generations differ even by 4 orders of magnitude (see below for a comparison with the mechanical results). It can also be noticed that with increasing generation the transitions become broader, which may be better seen in the differentiated DSC traces shown in Figure 2c with the **PG1s–PG4s** series as an example. Variation of both the glass transition temperature and the width of the transition with increasing dendron generation should be explained by the corresponding change of the molecular architecture. Increasing generation is, on one hand, related to an increase of the number of branching points, but, on the other hand, it involves an increase of the number of end groups. From the dynamic point of view, the branching will locally reduce the segmental mobility responsible for the glass transition, whereas the end groups will

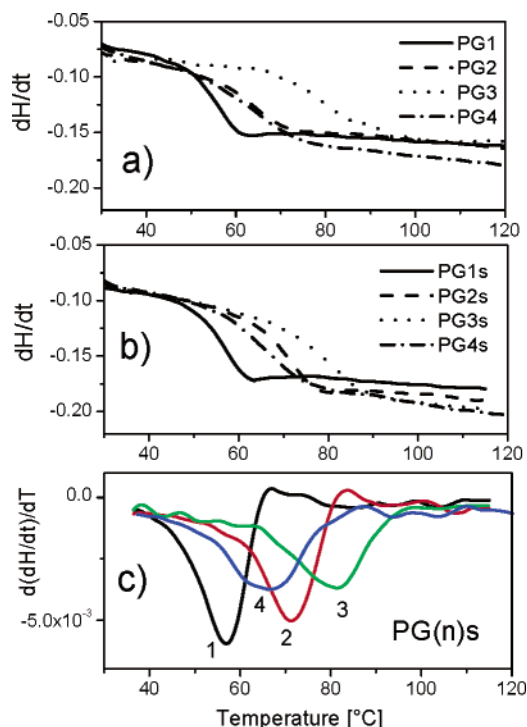


Figure 2. Second heating DSC thermograms for the dendronized polymers without (a) and with spacer (b and c). In (c), the differentiated traces are shown to better visualize the shift and broadening of the glass transition.

Table 2. Glass Transition Temperatures (T_g), Bulk Backbone–Backbone Spacing (d), and the Effective Backbone Length Per Repeat Unit (L_u) for Both Series of Dendronized Polymers **PG1–PG4** and **PG1s–PG4s**

polymers	T_g [°C]	d [nm]	L_u [nm]
PG1s^a	55.8	2.78	0.151
PG2s^b	71.4	4.03	0.155
PG3s^c	79.6	5.17	0.195
PG4s^d	68.2		
PG1^e	55.9	2.69	0.145
PG2^f	64.2	4.06	0.145
PG3^g	76.5	5.05	0.199
PG4^h	65.6	5.59	0.335

^a Entry 2 in Table 1. ^b Entry 3 in Table 1. ^c Entry 6 in Table 1. ^d Entry 7 in Table 1. ^e Entry 8 in Table 1. ^f Entry 9 in Table 1. ^g Entry 10 in Table 1. ^h Entry 11 in Table 1.

become more mobile. This can lead to a broader distribution of segmental relaxation times and consequently a broadening of the transition. This dynamic heterogeneity is probably also spatially nonuniformly distributed because the highly branched fragments of the repeat units are at least topologically closer to the polymer backbone than the free ends. Consequently, the probably cylindrically shaped macromolecules consist of the less mobile core around the backbone and more mobile periphery where elements of adjacent macromolecules interpenetrate each other to an extent which might be dependent on dendrimer generation. An increase of the glass transition temperature is generally related to a reduction of the segmental mobility. Consequently, the observed considerable increase of T_g for the first three generations should be related to a globally slower segmental dynamics. It can be conjectured that the increasing branching and additionally probably stronger segmental zipping at the more and more crowded dendron peripheries, which can be expected for higher generations, contribute to this effect. The observed increase of T_g with

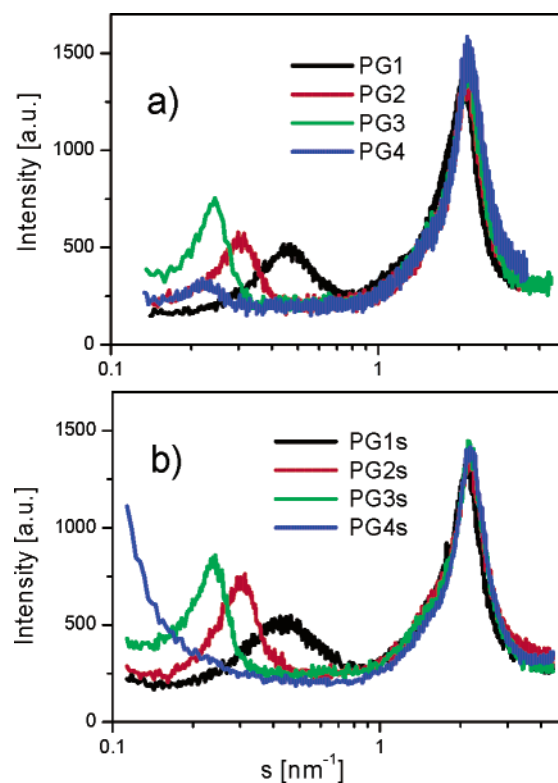


Figure 3. The X-ray diffractograms of (a) **PG(n)** and (b) **PG(n)s** series of samples.

increasing generation can be considered analogous to what has been reported by others for flexible dendrimers in bulk, for which the $1/M$ (M = molar mass) dependence was detected, indicating an increase to a limiting value at high molecular mass.⁸ The trend of increasing T_g also does not continue beyond G3 in the systems studied here. Both G4 homologues **PG4** and **PG4s** have an unexpectedly low T_g . This, however, may reflect their comparatively low degrees of polymerization (DPs of approximately 40) resulting in an effective reduction of the less mobile core fraction because of the naturally higher mobility at the backbone ends. This indicates that the problem of segmental mobility in the dendronized polymers becomes additionally related to the chain length. A separation of the effects resulting from variation of possible parameters (generation, spacer length, backbone length) would, however, require samples with better controlled molecular weights.

X-ray Diffraction. The polymers have an amorphous character; nevertheless, there are ordering effects, as detected by X-ray diffraction. Examples of X-ray diffractograms recorded at room temperature for samples of both series **PG1–PG4** and **PG1s–PG4s** are shown in Figure 3. Independent of the polymer, the diffractograms indicate an amorphous halo at wide angles and low angle peaks with positions, intensities, and widths depending remarkably on the size of the side groups. The wide angle halo seems to be asymmetric or consisting of two components. The more intensive maximum corresponds to real space distances of 0.4 nm, which can be attributed to spatial correlations between some repetitive elements such as the dendrons' phenyl rings. The peaks at low angles correspond to

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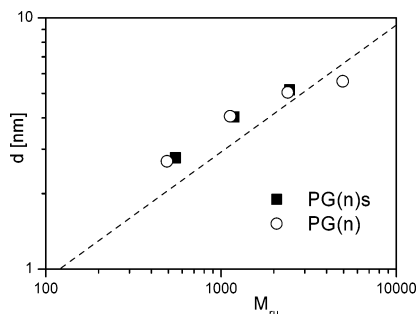


Figure 4. Dependencies of the backbone–backbone correlation distance on the molecular weight of the repeat units in the dendronized polymers. The dashed line represents a $d \sim M^{1/2}$ dependence for the maximally extended backbone. Different symbols correspond to dendrimer units with and without spacer.

distances exceeding one nanometer and in such amorphous systems reflect the thickness of the densely branched polymer.^{9,10} High spatial requirements of the bulky dendritic side groups probably make the backbone surroundings predominantly filled by elements of the same chain. This means the polymers can only weakly penetrate each other and consequently highly exclude each other in space.

This exclusion results in backbone–backbone distance correlations as well as correlations between end groups surrounding the cylindrical, but at higher temperatures still flexible, macromolecules. Both of these correlations can contribute to the low angle maxima in the recorded diffractograms and allow extraction of information related to the polymer thicknesses. Increasing intensities and decreasing width of the low angle peaks for generations increasing up to 3 confirm the above conjectures. This tendency seems, however, to break down at the fourth generation. In the system without spacer, only a considerable weaker low angle intensity peak is observed, and no intensity maximum at all in this range is detected for the samples with additional spacers. The values $d = K/s_{\max}$ are listed in Table 2 and can be considered as nearly reflecting the macromolecular diameters or the backbone–backbone distances. The constant K is not exactly known if the correlation does not extend over longer distances. Following the arguments of Guinier,¹¹ we assume here $K = 1.23$, which is usually considered for nearest neighbor correlations (for a hexagonal arrangement of locally oriented cylindrical chains, $K = 1.15$ should be taken, for example). The systems studied seem from any point of view to behave as amorphous. Therefore, larger scale order is not expected.

To understand the above results, let us consider that the backbone–backbone distance correlations d in a dense system are controlled by both the spatial requirements of the side groups (i.e., their sizes) and the backbone extension. For a backbone contour length not influenced by the side group's size, the dependence between d and the molar mass of the repeat unit (M_{ru}) should be $d \sim M_{\text{ru}}^{1/2}$, as a result of simple volume balance consideration at a constant bulk density. The macromolecule is regarded as a dense but flexible cylinder. This dependence is represented in Figure 4 by a dashed line. Both series of the

dendronized polymers seem to follow this relation for the two first generations but obviously deviate (Figure 4) for higher generations. Here, the d values increase slower with increasing M_{ru} than would take place at constant backbone extension. Qualitatively, this can be interpreted as an increasing backbone extension with increasing dendron size and means that more extended chains just thicken not as much with increasing side group volume. This suggests that higher extension and consequently higher effective stiffness of the backbone for higher generations must be considered.

Taking into account the molar masses of the repeat units (M_{ru}), the backbone–backbone distances (d) can be estimated as corresponding to a diameter of the cylindrical macromolecule which can be described as follows:¹⁰

$$d = 2\sqrt{M_{\text{ru}}/\pi\rho N_{\text{A}}l_{\text{ru}}} \quad (1)$$

where ρ is the polymer bulk density (here assumed $\rho = 1$, because of lack of an experimental value), N_{A} is the Avogadro constant, and l_{ru} is the length of the backbone per monomer. This dependence is shown in Figure 4 by a dashed line for the special case of fully extended backbone ($l_{\text{ru}} = 0.25$ nm) which represents the smallest possible diameter for a given M_{ru} . On the other hand, having determined d , it is possible to estimate the mean effective length of the backbone per repeat unit by means of the same relation. The corresponding values (l_{ru}) are listed in Table 2. They indicate that the chain extension increases very fast starting from G3 for which values are reached close to those expected for a completely extended backbone (0.195 and 0.199). For G4, in one case, no maximum is observed in the expected s -range (Figure 3b), and, in the other case, the peak's scattering intensity is relatively weak (Figure 3a). The corresponding s value translates into a backbone extension exceeding the accessible limit (0.34). This might mean that the fourth generation dendronized polymers of the given here architecture have already too large mass to be polymerized into long linear chains. Increasing packing problems result when the more and more bulky and compact macromonomers are anchored to the linear backbone one after the other. The presented structural effect seems to explain the observed limitations in achieving higher polymerization degrees for the macromonomers of the fourth generation. Short chains could still be possible because the intramolecular crowding can still to some extent be relaxed at chain ends. Theoretical¹² and experimental studies¹³ on the curvature of dendronized polymers are available.

Dynamic Mechanical Measurements. Despite their structured packing in the bulk, there is a considerable mobility in dendronized polymers as detected by means of dynamic mechanical measurements. They were characterized in a way typical for amorphous melts, that is, by means of master curves representing frequency dependencies of the real (G') and imaginary (G'') components of the complex shear modulus in a broad frequency range. This representation of the mechanical behavior reflects usually a spectrum of properties of materials at a chosen reference temperature in relation to various relaxation processes of molecular or supramolecular elements.

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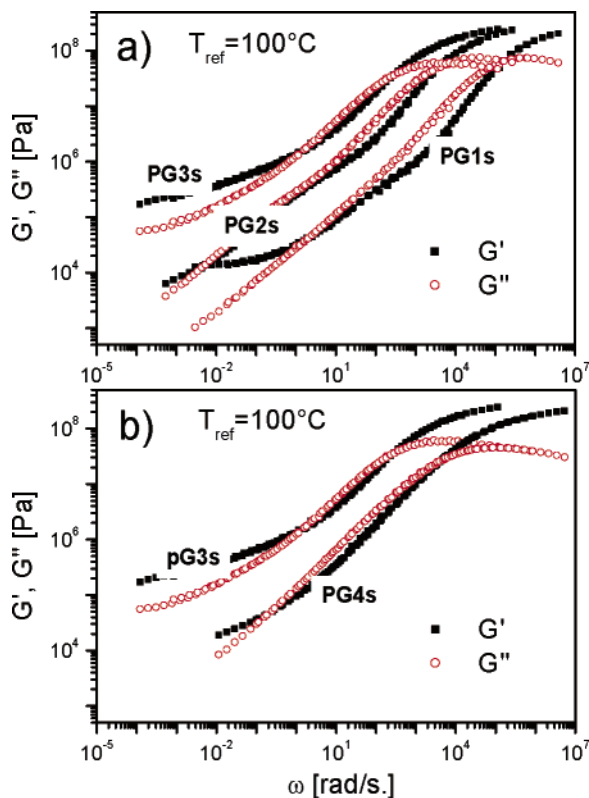


Figure 5. Frequency dependencies of the real (G') and imaginary (G'') parts of the complex shear modulus (master curves at a reference temperature $T_{\text{ref}} = 100\text{ }^{\circ}\text{C}$) for the dendronized polymers (a) generations 1–3 and (b) generations 3 and 4.

The properties may usually vary between those characteristic for the glassy state and those for a liquidlike state as indicated by the dynamic mechanical behavior at high and at low frequencies, respectively.¹⁴ Details of the behavior between these extremes depend on the molecular structure. Examples of the results of the dynamic mechanical characterization of the series of dendronized polymers at the common reference temperature of $100\text{ }^{\circ}\text{C}$ are shown in Figure 5.

As already observed in the DSC traces, the polymers have a glassy state. According to the mechanical tests, they are characterized in this state by modulus values exceeding 10^8 Pa (the plateaus at high frequencies). This range of the spectra corresponds to deformation rates (frequencies) which are faster than segmental mobilities of the polymers, and the cross points between G' and G'' observed at the low-frequency edges of these plateaus indicate the deformation rates which become comparable with the segmental relaxations. The results presented in Figure 5 indicate considerable differences in the segmental mobility between different samples which reflect the differences in the glass transition temperatures observed in the DSC. In Figure 6, the segmental relaxation times determined from the mechanical behavior of polymers are shown as a function of temperature and compared with temperatures of the glass transitions determined by DSC (full triangles). The results show that the segmental relaxation times in various polymers reach values of 10 s nearly at temperatures corresponding to the T_g values. This shows a good agreement between the mechanical and calorimetric observations. The increasing dynamic hetero-

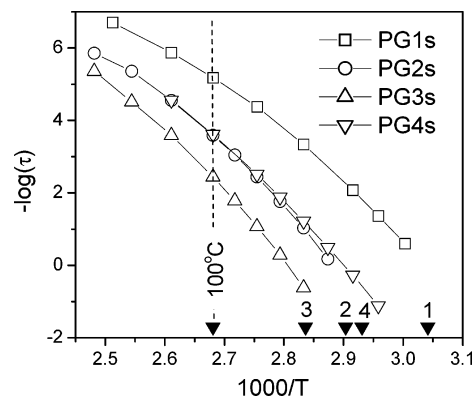


Figure 6. Temperature dependencies of the segmental relaxation times for the dendronized polymers of various generations. The arrows point toward T_g 's as detected by DSC. The vertical dashed line shows the reference temperature for the results of Figure 5.

geneity of the systems with increasing dendron generations is, as discussed earlier, also reflected in the mechanical spectra by a remarkable broadening of the segmental relaxation process. An attempt to characterize this broadening by means of the parameters of the Fourier transformed stretched exponential function, $\exp(-(t/\tau)^\beta)$, using just a graphical approximation, indicated that the exponent β decreases from the value of nearly 0.4 to a very low value of 0.2 between G1 and G4, respectively.

The mechanical spectra shown in Figure 5, when considered at deformation frequencies below the frequency at which the segmental relaxation is observed, can be correlated further with the parameters of the specific architecture of the polymers. These parts of the spectra can also be considered as reflecting behavior above the glass transition temperature when tested isochronically. In this range of testing conditions, the samples become viscoelastic with a broad spectrum of relaxations characteristic for each of them. Two parameters, the backbone length and the sizes of the anchored dendrons, determine this behavior. Unfortunately, these parameters in the studied samples do not change independently, and the G' and G'' dependencies are determined in a limited frequency range, because measurements at temperatures higher than $130\text{ }^{\circ}\text{C}$ led to irreversible changes of the structure and properties probably resulting from cross-linking. Above this temperature, the systems cannot be considered as rheologically simple. An example of such an effect is illustrated in Figure 7, in which the low-frequency part of the viscoelastic spectrum changes irreversibly with increasing temperature, indicating a formation of the rubbery state with modulus increasing with annealing temperature and time.

A common observation in the results presented in Figure 5 is that when the segmental relaxation starts, the modulus drops, however, in different ways for different samples. Taking into account the limited accessibility of the mechanical characteristics of these polymers, the low-frequency part of the observed properties can be understood on the basis of analogies of these polymers with other relevant systems such as brushlike polymers^{10,15,16} or stars.^{14,17} There are indications in the results presented in Figure 5 that for all polymers, there is a slower relaxation process which can be attributed to relaxations of the

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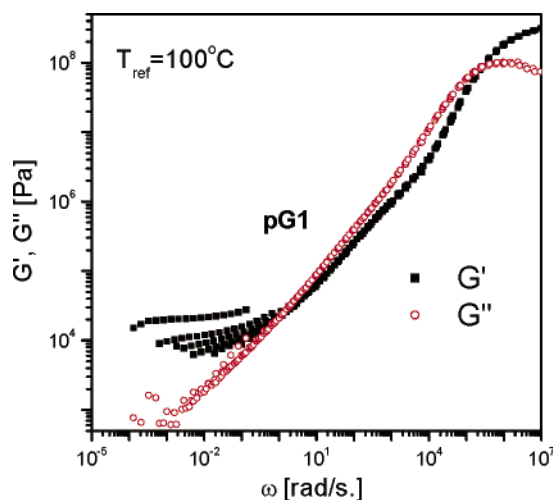


Figure 7. Frequency dependencies of the real (G') and imaginary (G'') parts of the complex shear modulus (master curves at a reference temperature $T_{\text{ref}} = 100\text{ }^{\circ}\text{C}$) for the dendronized polymer. At higher measurement temperatures, the system irreversibly changes properties (see the low-frequency plateau of G').

side groups. This relaxation can be characterized by a plateau of G' at a typical polymeric level (between 10^5 and 10^6 Pa) and by relaxation times becoming slower with increasing side group sizes. For the polymer **PG3s**, the G' stays above the level of 10^5 Pa up to the lowest seen frequencies, which can mean that this relaxation dominates the behavior becoming too slow to be observed in the accessible range.

Relaxation of the side groups leads to a further drop of the G' values, which is seen in polymers **PG1s** and **PG2s**, but only to the level of the order of 10^4 Pa which can be considered as controlled by the relaxation of the entangled backbones if sufficiently long. A flow is not observed in any of the samples, but the low-frequency G' plateau is more distinct for the **PG1** with a higher backbone length. The new G' plateau at the lowest frequencies means that the global polymer relaxation takes longer times. This terminal relaxation is not really observed in any of the systems studied here, but this seems to be limited by the instability of these systems for thermally induced cross-linking as indicated in Figure 7. The cross-linking seems to start at temperatures lower than those at which the chain relaxation would have an observable rate. The plateaus of G' observed for samples **PG1s** and **PG2s** at the lowest frequencies (Figure 5) are in the range that is characteristic for polymeric or colloidal systems with a large number of pendant groups.^{9,15–19} The behavior of **PG4s** cannot be precisely interpreted, but probably the small backbone length and high polydispersity are mainly responsible for the fast drop of G' despite the largest side groups. An exact analysis of the systems in the discussed frequency range would require polymers with comparable lengths of the backbones and possibly with a lower polydispersity, but first with polymers of higher thermal stability.

In the performed characterization of structure and dynamics, no remarkable differences have been detected for samples with and without spacers.

3. Conclusions

The thermally induced radical polymerization of the G1–G4 dendronized methacrylate macromonomers **3**, **5**, **7**, and **9** with a methyleneoxycarbonyl spacer gave the corresponding

dendronized polymers **PG1s–PG4s** as analytically pure materials. The first three members of this homologous series exhibit high molar masses. The G4 monomer still gave high oligomers in high yield. This series of polymers was compared with an already existing one (**PG1–PG4**), which lacks this spacer, to find out whether the spacer has an effect on polymerization behavior. As judged by the factors of total polymerization time, yield, and molar mass, no significant difference was observed between these two series. This indicates that in cases where a spacer effect was proposed other reasons should also be taken into consideration.

Analysis of the structure of the dendronized polymers **PG1–PG4** and **PG1s–PG4s** in bulk indicates backbone–backbone distance correlations giving rise to a distinct small angle peak in the X-ray scattering intensities, however, without any signatures of a longer range order as that suggested for systems studied by others.^{20,21} The correlation improved with increasing generation up to G3 but was almost lost for G4. Considering the detected correlation distances under the condition of dense packing of polymers in bulk leads to the conclusion that anchoring of bulky dendrons to the backbone with a high grafting density results in backbone extensions. These extensions increase drastically for the higher generations (G3 and G4). In the case of the highest studied generation (G4), the packing problems seem to impose limits on the growth process so that high numbers of repeat units cannot be reached. Probably because of the small length of the methyleneoxycarbonyl spacer, there are no significant differences between the samples with and without spacer.

Analysis of the dynamics in the studied systems indicates remarkable effects of the polymer architecture on the segmental relaxation controlling the transition to the glassy state. Increasing the dendron generations led to a considerable increase of the temperature of the materials' main softening. This temperature increase is equivalent to a slowing down of the segmental relaxation, when the different polymers are compared at a given temperature. This observation was in good agreement with DSC results. Here, the increase of the dendron generations involved also a considerable broadening of the segmental relaxation process, indicating an increasing dynamic heterogeneity of the systems. Above the glass transition, the viscoelastic properties are dominated by either side group or backbone relaxation depending on the sizes of these structural elements. In the case of the longer chains with the smaller G1 and G2 dendrons, the side group relaxations are relatively fast, and the low-frequency G' plateaus at the level of 10^4 Pa are indicative of nonrelaxed backbones. For the more internally crowded and extended polymers with G3 dendrons, the behavior was controlled by the nonrelaxed side groups. This was concluded because the low-frequency plateau remained on the level exceeding 10^5 Pa. Unfortunately, the thermal instability of the systems at temperatures higher than $130\text{ }^{\circ}\text{C}$ made impossible a comprehensive analysis of the polymers' dynamic behavior up to the flow range.

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Also, in the dynamics and resulting properties, no effect of the short spacer has been observed.

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Supporting Information Available: All synthetic procedures and analytical data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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