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^{1}H and ^{13}C NMR Spectra of Highly Branched Poly(4-chloromethylstyrene). Signal Assignment, Structure Characterization, and a SCVP Kinetics Study

Hartmut Komber,* Ulrike Georgi, and Brigitte Voit

Leibniz Institute of Polymer Research Dresden, Hohe Strasse 6, D-01069, Dresden, Germany

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ABSTRACT: In this work, we present a detailed structural analysis of poly(4-chloromethylstyrene) (P(4-CMS)) by 1D and 2D NMR methods. A signal assignment and quantitative analysis of the different aliphatic structures of the polymer backbone were achieved. Combining signal integration of spectra taken in both C_6D_6 and CD_2Cl_2 as solvent, the content of terminal (T), vinyl-type linear (L_V), condensation-type linear (L_C), and dendritic (D) units and thus the degree of branching could be determined. The study is completed by a kinetics study of the polymerization of 4-CMS at 115 °C in chlorobenzene with CuCl/bpy as activator. The development of subunits is followed depending on vinyl group conversion and compared with a theoretical study of Müller et al. Obviously, the fractions of structural units cannot be predicted by a simple theoretical model due to the complexity of the mechanism of the atom transfer radical polymerization (ATRP). An increased content of L_V units is rationalized by both a retarded deactivation resulting in multiple monomer addition steps and a higher reactivity of the secondary radical compared with the primary one.

Introduction

Since first studies in the 1980s, hyperbranched or highly branched polymers have been the subject of a growing number of investigations. A vast variety of chemical structures and polymer architectures have been synthesized by different strategies and an increasing number of potential and realized applications have been demonstrated.[1−4] One of the basic synthetic strategies is the self-condensing vinyl polymerization (SCVP) first applied intentionally for the synthesis of hyperbranched polymers by Fréchet et al. in 1995.[5] This polymerization is based on a monomer bearing both a vinyl group (**A**) and an initiating group (**B***). Depending on the nature of the monomer, various types of living polymerization, i.e. cationic, radical, group transfer, and even ring-opening polymerization, have been adopted for SCVP. Different approaches have been developed to vary the overall polymer architecture, e.g., by copolymerization with a conventional monomer, by addition of multifunctional core molecules, or by using **AB***-type macromonomers.

Immediately after first experimental work, Matyjaszewski et al.[6,7] and Müller et al.[8,9] extensively studied the mechanism and kinetics of SCVP and treated the molecular parameters of hyperbranched polymers and copolymers[10,11] made by SCVP theoretically. Recently, the Monte Carlo method was applied to include steric effects and intramolecular cyclization in the simulation of SCVP[12] and the kinetics of SCVP with nonequal concentration of stimulus and monomer was theoretically studied by Zhou and Yan.[13]

Müller coined the word inimer (=initiator + monomer) for SCVP monomers[8] and developed schemes showing the possible structures formed from **AB*** polymerization.[9] These monomers allow step growth polymerization by addition of the initiating site **B*** with the double bond **A** forming propagating sites **A*** (Scheme 1a). **A*** can add a monomer vinyl group (**A**) in a chain growth polymerization. Concurrence of both polymerization mechanisms results in the hyperbranched structure with one focal unit (F) and the characteristic dendritic (D), linear (L), and terminal (T) units. The terminal units have both an **A*** and a **B*** functionality as reactive sites which can react with a vinyl group **A** to form vinyl-type linear unit L_V (**A*** + **A**) or a condensation-type linear unit L_C (**B*** + **A**). Both terms were introduced by Müller et al. because L_v resembles a monomer unit of a vinyl polymer and L_C a repeating unit of a polycondensate[9] as also illustrated by the decamer structure given in Scheme 2.

A priori, one cannot expect equal reactivity for the initiating (**B***) and propagating (**A***) sites. The reactivity ratio has a considerable effect on the degree of branching (DB) as a characteristic molecular parameter of hyperbranched polymers.[9] Generally, the DB can be calculated from the content of the D, L, and T units,[8,9] which are mostly determined by quantitative NMR spectroscopy based on careful signal assignment. As (meth)acrylates and styrenes are typical inimers used in SCVP, the signal splitting due to D, L, and T units is superposed by the splitting due to the tacticity of the backbone. Therefore, in contrast to many other hyperbranched polymers based, e.g., on polycondensation or polyaddition reactions, the analysis of the NMR spectra of hyperbranched SCVP polymers with respect to quantifiable signals of these subunits often failed.

The first SCVP was described for 3-(1-chloroethyl)-ethenylbenzene as **AB*** monomer based on a cationic mechanism.[5] The SCVP based on metal complex-mediated atom transfer radical polymerization (ATRP) mechanism (Scheme 1b) of a similar inimer, 4-chloromethylstyrene (4-CMS), was first reported by Gaynor et al.[14] and intensively studied by Weimer et al.[15] They characterized the highly branched poly(4-chloromethylstyrene) (P(4-CMS)) by ^{1}H and ^{13}C NMR spectroscopy and concluded from the signal assignments that a conclusive determination of the degree of branching is not possible. Therefore, a value of the minimum percent linearity was defined.

P(4-CMS) was used as the multicenter initiator in the synthesis of dendrigraft polymers by ATRP.[16,17] Furthermore, 4-chloromethylstyrene was widely applied as inimer in the ATR SCV

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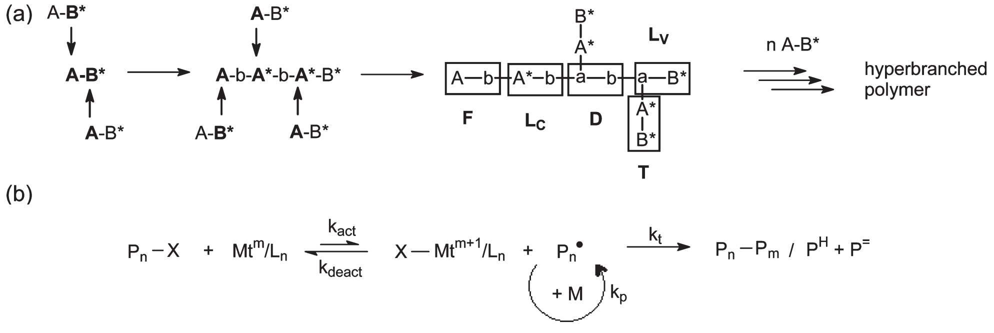
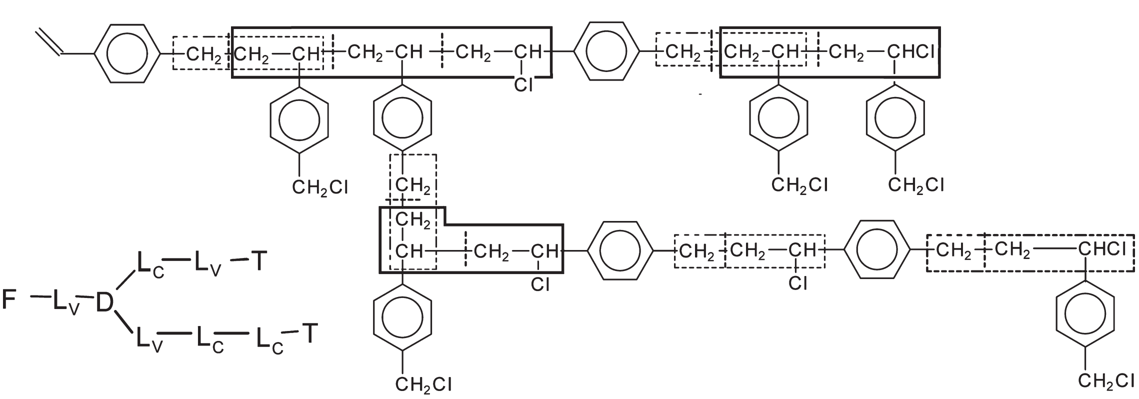
*To whom correspondence should be addressed. Telephone: +49 351 4658 343. Fax: +49 351 4658 565. E-mail: komber@ipfdd.de.

Scheme 1. (a) Structure Formation in the Self-Condensing Vinyl Polymerization of an AB* Monomer by (A + B*) and (A + A*) Addition Steps Resulting in the Typical Subunits of Such a Highly Branched Polymer: Focal (F), Terminal (T), Vinyl-Type Linear (L_V), Condensation-Type Linear (L_C), and Dendritic (D) and (b) Mechanism of Metal-Complex-Mediated ATRP (P, Polymer Chain; X, Cl or Br; Mt^m, Transition Metal; L, Complexing Ligand; M, Monomer; k_{act}, k_{deact}, k_p, and k_t, Rates of Activation, Deactivation, Propagation, and Termination, Respectively)



Scheme 2. Chemical and Schematic Structure of a Decamer from SCVP of 4-Chloromethyl Styrene[a]



[a] The ten monomer units are separated by a dashed vertical line. Backbone sections of condensation-type are marked by dashed boxes, vinyl-type sections by solid boxes.

copolymerization to synthesize branched polymer structures, e.g., with *N*-cyclohexylmaleimide,[18] chlorotrifluoroethylene,[19] styrene,[20] and pentafluorostyrene.[21]

The SCVP of 4-CMS by ATRP under various conditions was applied in our group to synthesize highly branched P(4-CMS) with different molecular weights. It could be shown that this hyperbranched polymer based on an easily available monomer offers a promising scaffold for polymer-analogous reactions, e.g., for hydrogenation to obtain hyperbranched poly(4-methylstyrene) and for substitution of the chloro group to introduce new functionalities in hyperbranched polystyrenes.[22]

In the course of these studies, the structure characterization of parent highly branched poly(4-chloromethylstyrene) was undertaken by NMR spectroscopy. Thereby, it became obvious that few but significant assignments given by Weimer et al.[15] need revision. This paper reports on the ^1H and ^{13}C NMR signal assignment of highly branched poly(4-chloromethylstyrene) by combination of 1D and 2D NMR methods and on an approach to determine the degree of branching of these polymers. The structure development in dependence on vinyl group conversion is discussed based on a kinetics study.

Experimental Section

Polymers. The highly branched poly(4-chloromethylstyrene) samples **1** (Table 1) were prepared from 4-CMS by ATRP applying different approaches. Besides the classical synthesis with CuCl/bipyridine activator in chlorobenzene as solvent[15] the activators generated by electron transfer (AGET) method[23] was used. Table 1 summarizes important synthesis conditions and molecular parameters of the samples used in this NMR study. The synthetic procedures are described in detail in the Supporting Information. The gel permeation chromatography (GPC) data were determined on a modular built system coupled with a multiangle laser light scattering and a refractive index detector using THF as solvent and a sample specific calibration. The linear P(4-CMS) sample **2** was synthesized from 4-CMS by reversible addition−fragmentation chain transfer (RAFT) polymerization using 4-cyano-4-(thiobenzoylthio)pentanoic acid as chain transfer agent and 4,4′-azobis(4-cyanovaleric acid) as initiator as described in the Supporting Information.

NMR Measurements. ^1H (500.13 MHz) and ^{13}C (125.74 MHz) NMR spectra were recorded on a Bruker DRX 500 spectrometer using a 5 mm $^1H/^{13}C/^{19}F/^{31}P$ gradient probe at 303 K. The NMR spectra were referenced on signal of the solvent used (^1H, 7.26 ppm ($CDCl_3$), 7.16 ppm (C_6D_6), 5.31 ppm (CD_2Cl_2); ^{13}C, 77.0 ppm ($CDCl_3$), 128.7 ppm (C_6D_6)).

The ^1H NMR spectra were recorded using 90° ^1H pulses, an acquisition time of 2.73 s and a delay time of 10 s. The quantitative ^{13}C NMR spectra were recorded using the inverse-gated pulse sequence, 90° ^{13}C pulses, and a delay time of 10 s. The $^1H-^1H$ correlation spectra (gs-COSY, TOCSY), the $^1H-^{13}C$ correlated spectra (gs-HMQC, gs-HMBC) and the DEPT135 spectra were recorded using the pulse sequences in the Bruker software package.

^1H and ^{13}C Substituent Chemical Shifts. Substituent chemical shifts (SCS) of the chloromethyl, 1-chloroethyl, *n*-propyl, and isopropyl groups were determined from $CDCl_3$ solutions of the corresponding monosubstituted benzenes (Table S1, Supporting Information). The SCS values were calculated using 7.16 ppm (^1H) and 128.5 ppm (^{13}C) as ^1H and ^{13}C reference benzene shifts.

Results and Discussion

Evaluation of the General Polymer Structure. Before discussing the experimental NMR spectra a general view on the substructures realized in a highly branched

Table 1. Synthesis Conditions and Structural Parameters of Poly(4-chloromethyl styrene) Samples

run	[Cu]/[4-CMS]	T [°C]	t [h]	$M_{n,NMR}$ [g/mol]	$M_{n,GPC}$ [g/mol]	PDI	T[a] [%]	L_V[a] [%]	L_C[a] [%]	D[a] [%]	DB_{Frey}[a] [%]
1a[b]	0.02	110	2.5	2750	3850	3.30	21	43	13	23	45
1b[c]	0.05	115	5	5500	5000	3.64	15	14	49	22	41
1c[d]	0.10	115	6	6800	7800	4.74	17	22	35	26	48
1d[d]	0.15	115	5	7100	6400	4.30	16	20	39	25	46
1e[e]	0.02	115	9	3400	3700	2.92	20	25	30	25	48
1f[e]	0.05	115	6	3800	4100	4.58	18	25	33	24	45
1g[e]	0.10	115	6	4700	6600	5.85	16	21	36	27	49

[a] Absolute error: ≤ 2% [b] Classic ATRP in bulk. [c] Tris[(2-pyridyl)methyl]amine (TPMA) instead of bpy as copper ligand. [d] Classic ATRP in chlorobenzene. [e] AGET ATRP in chlorobenzene.

poly(4-chloromethylstyrene) is helpful. Scheme 1a gives a schematic picture of a SCVP polymerization from **AB*** monomers, whereas Scheme 2 depicts a decamer of 4-chloromethylstyrene with highlighted substructures. The structure is based on head-to-tail addition of vinyl groups as observed for polystyrenes and on solely intermolecular addition reactions. Thus, each macromolecule bears one focal vinyl group. The two different polymerization reactions, i.e., addition of **A** to **A*** and addition of **A** to **B*** functionalities, result in two basic backbone substructures. The first reaction results in the $-CH_2-CHAr-CH_2-CHArX$ substructure (X = Cl) and after further addition of **A** groups on the $-CHArX$ site it results in longer sequences containing units with X = CH_2. These substructures are typical for vinyl polymers and highlighted in Scheme 2 by solid boxes. The two methine groups can result in a *meso* (*m*) or *racemic* (*r*) dyad. Longer sequences can be *isotatic*, *atactic*, or *syndiotactic*. The NMR chemical shifts of these substructures reflect effects over several bonds, i.e. between several subunits, and a signal assignment to a certain subunit is unlikely, also because the NMR signals for polystyrenes are typically broadened. The addition of a vinyl group to an $Ar-CH_2Cl$ group results in a $-CH_2-CH_2-CHCl-$ substructure isolated between two aromatic rings and without different isomers (dashed boxes in Scheme 2). As it resembles a repeating unit in a polycondensate, the corresponding linear unit is denoted as L_C.[9] Two subunits contribute to this substructure in a dyad which is determined by the *para*-substitution of the aromatic rings; L_C-T, $D-T$, L_C-L_C, and $D-L_C$ are the possible dyads. A ^{13}C chemical shift effect of the different *para* substituents over five or six bonds is expected to be very small and discrimination between the four dyads seems to be unlikely. The second units in these dyads (T, L_C) can initiate chain growth; after addition of a vinyl group the substructure $-CH_2-CH_2-CH(CH_2-)-$ is formed with the methine carbon as a part of a vinyl type dyad (overlap of dashed and solid boxes in Scheme 2).

The substitution of chlorine by methylene results in distinct chemical shift effects for the α- and β-CH_2 groups but the overall structure becomes still more complicated. Therefore, the backbone signals should result in quite complex NMR signal regions. However, the chloromethylene ($-CHCl-$) and chloromethyl ($-CH_2Cl$) signals should be well separated from the other aliphatic signals due to the deshielding NMR effect of chlorine. One can distinguish chloromethylene groups for the $-CHAr-CH_2-CHArCl$ structure and the $Ar-CH_2-CH_2-CHArCl$ structure. Both are bonded to a phenyl ring with *para*-substitution. Depending on whether the *para*-chloromethyl group has reacted or not a further differentiation is possible. Similarly, different phenyl substitution in *para*-position to the chloromethyl group ($-CH(CH_2)_2$ vs $-CH(CH_2)Cl$) creates two chloromethyl groups. For the *para*-substituted phenyl units different combinations of $-CH(CH_2)_2$, $-CH(CH_2)Cl$, $-CH_2CH_2$, and $-CH_2Cl$ substituents are possible as depicted in Scheme 2.

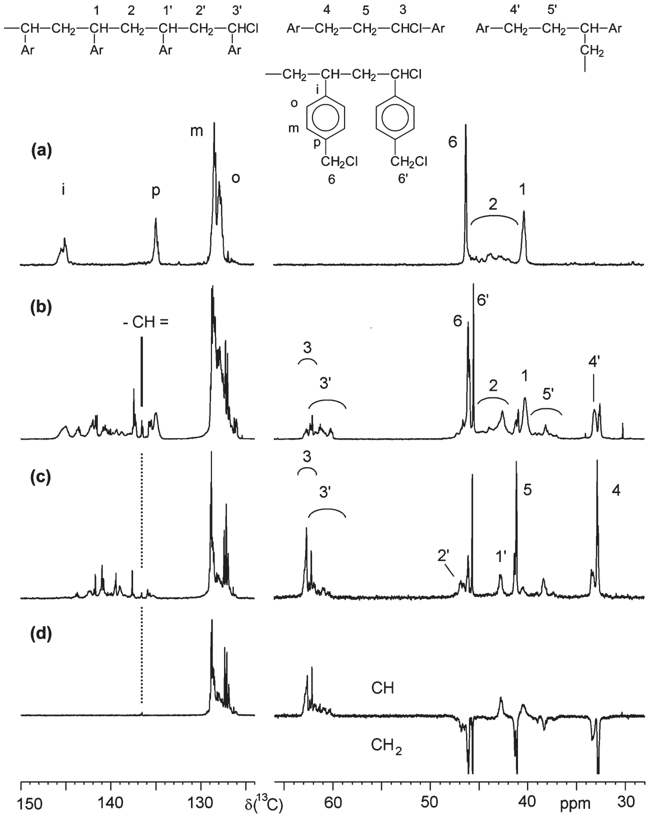


Figure 1. ^{13}C NMR spectra of a linear poly(4-chloromethylstyrene) (**2**, 100% L_V units) (a) and two highly branched poly(4-chloromethylstyrene)s with 43% L_V units (b, sample **1a**) and 14% L_V units (c, sample **1b**). The DEPT135 spectrum of sample **1b** is given as part d. The solvent is $CDCl_3$.

The ^1H and ^{13}C chemical shift effects of these substituents on the aromatic protons and carbons were determined from appropriate model compounds (Table S1, Supporting Information) and ^{13}C chemical shifts for the different structures were predicted (Table S2, Supporting Information). However, overlapping NMR signals of aromatic protons and carbons have to be expected.

^1H and ^{13}C NMR Signal Assignment. Two highly branched P(4-CMS) samples with different content of T, L_V, L_C, and D units (**1a**, **1b**) and the linear P(4-CMS) **2** were selected from a sample pool to deduce the ^1H and ^{13}C signal assignments. The determination of the content of T, L_V, L_C, and D units is exemplified in the next chapter based on the signal assignments but it is necessary to anticipate some results to make the discussion of the spectra easier.

Figure 1 depicts the ^{13}C NMR spectra of these three polymers. The signal assignment for the linear polymer **2** which is a model for a longer sequence of vinyl-type L_V units in a highly branched P(4-CMS) is straightforward (Figure 1a).

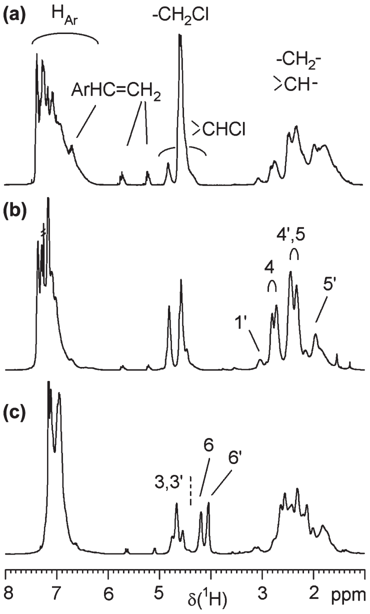


Figure 2. ^{1}H NMR spectra of **1a** (a) and **1b** (b) in $CDCl_3$ and of **1b** in C_6D_6 (c).

Similar to polystyrene, the methylene carbon shows significant signal splitting due to the atactic backbone but the methine and the chloromethyl carbon signals are narrow. The aromatic carbons C_i and C_p are well separated and also the C_o and C_m signals can be assigned. Characteristic features of this spectrum are also pronounced in the spectrum of **1a** with 43% L_V and 13% L_C units (Figure 1b) allowing first signal assignments. These signals diminish in the spectrum of **1b** (Figure 1c; 14% L_V and 49% L_C units). The new signal group at 60−64 ppm is caused by the chloromethylene groups. Accordingly, it appears as positive signal in the DEPT135 spectrum of **1b** (Figure 1d).

The signal pattern is complex but from the intensity changes going from the L_V-rich to the L_C-rich sample one can conclude that the diminishing high-field part is caused by $C_{3'}$ whereas the increase in the low-field part is caused by C_3. A further signal group not present in the linear P(4-CMS) appears at 32−34 ppm. The observed negative DEPT signals and their chemical shifts allow the assignment of this signal group to the $Ar-CH_2-$ methylene carbons (C_4; $C_{4'}$) in the $Ar-CH_2-CH_2-CHX-Ar$ substructures (X = Cl, CH_2). Within this region the broader signal centered at 33.3 ppm can be assigned to substructures with X = CH_2 ($C_{4'}$) involved in vinyl-type sequences and the narrower signals at 32.8 ppm can be assigned to the isolated structures with X = Cl (C_4). In an analogous manner the broad signal at 38.3 ppm and the narrower signals at 41.1 ppm can be assigned to the central methylene carbon of the $Ar-CH_2-CH_2-CHX-Ar$ substructure with X = CH_2 and X = Cl, respectively. A third pair of methylene signals appears at 46.1 and 45.6 ppm. Caused by the chloromethyl group the low-field signal is due to the L_V unit (C_6) whereas the neighboring units cause a fine splitting. $C_{6'}$ of the T units is represented by the high-field signal. Decreasing content of L_V units in the P(4-CMS) results in shorter vinyl-type sequences, a lower variety in configurations and is accompanied by an increased content of more or less isolated dyads of $-CHAr-CH_2-CHArCl$ structure. In the ^{13}C NMR spectra this is well reflected for the signals of methylene carbons. These signals cover the 41−46 ppm region for linear P(4-CMS) **2** with only L_V units but diminish with decreasing L_V content (**1a**, **1b**) and a new signal group, which is distinctly low-field shifted and narrowed, evolves at 46−48 ppm (Figure 1c,b). Simultaneously, the methine signal at 40.4 ppm decreases and a new methine carbon signal grows at 42.8 ppm which is assigned to the nonhalogenated methine carbon $C_{1'}$ in the aforementioned structure.

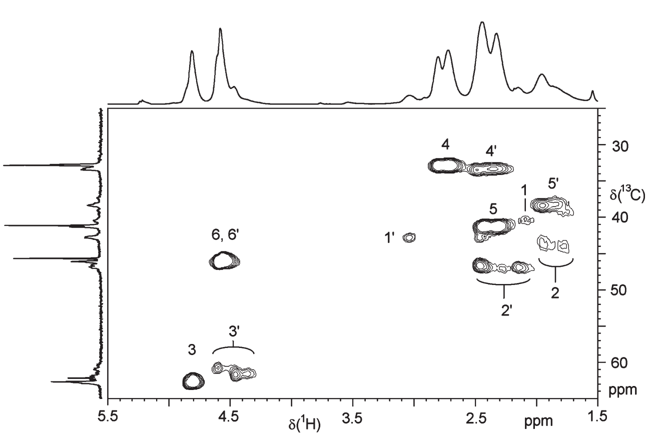


Figure 3. HMQC spectrum of the L_C-rich sample **1b** (solvent: $CDCl_3$).

Finally, the aromatic carbons region is subject of significant changes (Figure 1). Table S2 (Supporting Information) gives estimated shift values for the different carbons in the four subunits. It is obvious that a signal assignment to the *ortho* and *meta* carbons covering the 126−129 ppm region is pointless due to the signal overlap. The *ipso* and *para* carbons cover a broader chemical shift range but also here signals of different subunits overlap (cf. Table S2). Nevertheless, it should be pointed out that, going from **1a** with a high content of vinyl-type substructures to **1b** with a lower content of these, a decrease of broadened signals goes along with an increase of narrower signals. The vinyl group signals of the focal group appear at 112.9 and 113.2 ppm (=CH_2, not shown) and 136.5 ppm (−CH=).

Representative ^{1}H NMR spectra of highly branched P(4-CMS) are shown in Figure 2. The ^{1}H NMR signal assignment is tackled for **1b** in $CDCl_3$ (Figure 2b) by analyzing the corresponding heteronuclear multiple quantum coherence (HMQC) spectrum given in Figure 3 using the ^{13}C signal assignments. The aromatic CH region is not depicted in Figure 3 because the crowded ^{13}C signals are not assigned. From the HMQC spectrum it is obvious that the chloromethylene proton signals (H_3/$H_{3'}$) cover the full 4.2−4.9 ppm region whereas the chloromethyl proton signal is located right in the middle at 4.6 ppm. It cannot be distinguished between H_6 and $H_{6'}$.Weimer et al. assumed that both signal groups (H_3/$H_{3'}$ vs. H_6/$H_{6'}$) are separated allowing the determination of a $CHCl/CH_2Cl$ ratio by selective integration.[15] Probably, the quality of their HMQC spectrum did not allow to identify the weak cross peaks in the 4.2−4.7 ppm region. Therefore, such a ratio cannot be determined from the spectra taken in $CDCl_3$. However, both structures result in separated signal regions using C_6D_6 as solvent (Figure 2c). This spectrum will be discussed later on in the context of DB calculation. Turning back to the spectra taken in $CDCl_3$, the signal pattern in the 4.2−4.7 ppm region (Figure 3) is characteristic for vinyl polymers and should be caused by $H_{3'}$. The narrower signal at ∼4.8 ppm is due to methine protons H_3. It is obvious from the HMQC spectrum that the corresponding carbon signals are the more low-field shifted ones as claimed above but they are not fully separated from the vinyl−type CHCl carbon signals. The 1.5−3.2 ppm signal region of the ^{1}H NMR spectra is characterized by overlapping signals and less suited for a structure characterization.

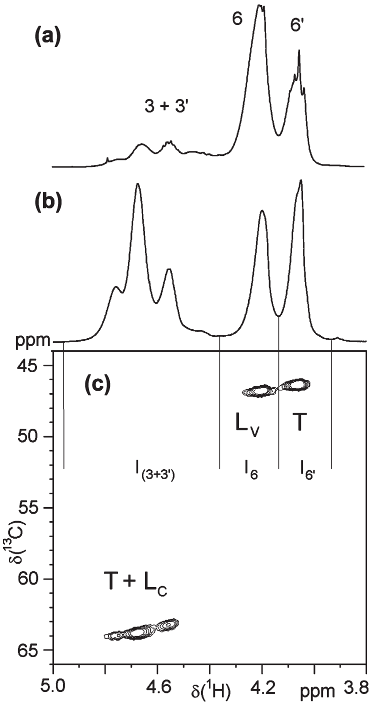


Figure 4. ^1H NMR spectra (region of CHCl and CH_2Cl protons) of **1a** (a) and **1b** (b) and HMQC spectrum (region) of **1b** (c). Solvent: C_6D_6.

Signal separation in the HMQC spectrum allows discriminating between the different contributions to the observed signal pattern. For **1b**, the signals with the highest intensity levels are due to the Ar$-CH_2-CH_2-$CHX$-$Ar methylene groups. As the methine carbon is asymmetric the methylene group protons are diastereotopic and result in signal pairs at 2.72 and 2.81 ppm (H_4) and 2.33 and 2.45 ppm (H_5) for X = Cl. The effect is less pronounced for X = H and results in rather broadened signals at 2.2$-$2.6 ($H_{4'}$) and 1.7$-$2.05 ppm ($H_{5'}$). With increasing content of L_V units, broadened signals of the vinyl-type structures (solid boxes in Scheme 1) dominate this region (Figure 2a).

Finally, the signals of the focal vinyl group functionality appear at 5.21 and 5.71 ppm ($=CH_2$) as well as at 6.73 ppm ($-$CH$=$). Termination and side-reactions can result in further structures. The existence of Ar$-CH_3$ groups formed from the benzylic radical by proton abstraction could be proved by the corresponding methyl signal in the ^1H and ^{13}C NMR spectra (2.31 ppm; 21.1 ppm; not shown). Structures formed from the **A*** based radical by proton abstraction as well as by biradical coupling should also occur. The ^{13}C signals of the first are expected in the 35 ppm region overlapping with more intense signals of the backbone. ^{13}C NMR signals from structures formed by coupling of two $-CH_2PhH^*$ chain ends were assigned in the 47$-$52 ppm region for polystyrene ^{13}C-enriched in CH position.[24] However, the ^{13}C NMR spectra are too noisy to prove signals of very low intensity in this region, but, biradical coupling reactions should become noticeable in the molecular weight distribution by high-molecular-weight fractions. Finally, the elimination of HCl from the Ar$-CH_2-CH_2-$CHCl-Ar substructure was proven. The resulting structure Ar$-CH_2-$CH$=$CH$-$Ar can be identified in the ^1H NMR spectrum by a characteristic signal group between 6.2 and 6.5 ppm ($-$CH$=$CH$-$) and a broadened signal at 3.55 ppm for the methylene group (see Figure S1).

The ^1H and ^{13}C signal assignments are confirmed by TOCSY and HMBC measurements (Figures S1 and S2, Supporting Information). ^{13}C and 2D NMR spectra of **1b** dissolved in C_6D_6 are given in the Supporting Information (Figures S3$-$S7). The spectra are very similar to those recorded in $CDCl_3$ and the ^{13}C NMR signals can be assigned as discussed in this chapter for $CDCl_3$ solution.

Quantitative Structure Characterization. The quantification of structural units in highly or hyperbranched polymers by NMR spectroscopy is based on signal integrals which are related to the content of the different subunits, i.e. to dendritic (D), linear (L), and terminal (T) units. Usually, ^1H NMR is preferred because quantitative spectra can be obtained with a low amount of substance within short time. Thus, the content of T, L, and D units and thus DB could be calculated for highly branched poly(4-iodomethylstyrene) having a structure very similar to P(4-CMS).[25]

As outlined by Weimer et al.[15], the ^1H NMR spectrum of highly branched P(4-CMS) taken in $CDCl_3$ does not provide appropriate signal integrals due to signal overlap. Furthermore, the value of the minimum percent linearity calculated from the CHCl/CH_2Cl ratio by these authors can not be considered correct since they overlooked the signal overlap of CHCl and CH_2Cl signal as outlined in the preceding section.

Fortunately, we found that highly branched P(4-CMS) results in a satisfying signal separation in the CHCl and CH_2Cl protons region when C_6D_6 is used as solvent (Figure 2c, Figure 4).

Such aromatic solvent induced shifts (ASIS) in ^1H NMR spectra are well-known from the beginnings of NMR spectroscopy.[26] The three integral regions, i.e., $I_{(3+3')}$, I_6, and $I_{6'}$, indicated in Figure 4c allow to determine integral equivalents for one proton in T, L_V, and L_C units:

$$I(\mathrm{T}) = I_{6'}/2 \tag{1}$$

$$I(\mathrm{L_V}) = I_6/2 \tag{2}$$

$$I(\mathrm{L_C}) = I_{(3+3')} - I(\mathrm{T}) \tag{3}$$

Each kind of subunit contains nine protons. Thus, the integral equivalent for one proton in D units, I(D), can be calculated from the integral equivalent for one proton in a repeating unit of the polymer, I(rep), subtracting the values of I(T), $I(L_V)$, and $I(L_C)$. There are two reasonable possibilities to calculate the integral intensity of one proton in the repeating unit. First, the total integral of all aliphatic protons divided by 5 gives I(rep). For low-molecular-weight products also the vinyl protons integrals have to be added. However, signals from impurities appearing in this broad region can falsify the integral. Therefore, we preferred to integrate all aromatic protons in order to determine I(rep). Unfortunately, in C_6D_6 solution this integral is falsified by the residual solvent signal and, therefore, the sample had additionally been measured in a second solvent. CD_2Cl_2 is a good choice because there is no overlap of the residual solvent signal with either the aromatic protons or the CHCl/CH_2Cl region. The integral value of the CHCl/CH_2Cl region is the intensity reference to compare the integrals from spectra in different solvents. With the integral of all aromatic protons, I_{Ar}, I(D) can be calculated as follows:

$$(I(\mathrm{D}) = (I_{\mathrm{Ar}}/4) - I(\mathrm{T}) - I(\mathrm{L_V}) - I(\mathrm{L_C})) \tag{4}$$

In particular, for low-molecular-weight compounds, the I_{Ar} value has to be corrected for the signal intensity of one vinyl proton overlapping at about 6.7 ppm. This intensity,

I(vinyl), can be taken from the integral value of one $=CH_2$ proton.

It is obvious that I(D) is faultier than the other intensity values but accurate enough to allow conclusions with respect to the branched structure of P(4-CMS) from the degree of branching (DB) calculated according to the equation of Frey:[27]

$$\mathrm{DB}_{\mathrm{Frey}} = 2I(\mathrm{D})/(2I(\mathrm{D}) + I(\mathrm{L_V}) + I(\mathrm{L_C})) \qquad (5)$$

Assuming that each polymer molecule bears one focal group, the degree of polymerization, $\mathrm{DP_n}$, and the number-averaged molecular weight, $M_{\mathrm{n,NMR}}$, can be estimated from I(vinyl) and I(rep):

$$\begin{aligned} M_{\mathrm{n,NMR}} &= \mathrm{DP_n} \times 152.6\ \mathrm{g\ mol^{-1}} \\ &= I(\mathrm{rep})/I(\mathrm{vinyl}) \times 152.6\ \mathrm{g\ mol^{-1}} \qquad (6) \end{aligned}$$

To illustrate the usability of this procedure, Table 1 summarizes the content of T, $\mathrm{L_V}$, $\mathrm{L_C}$, and D units, $\mathrm{DB_{Frey}}$s and M_n values for several highly branched P(4-CMS) samples synthesized under different experimental conditions. The fractions of these units in a SCVP with equal and nonequal rate constants of initiating (**B***) and propagating (**A***) centers were theoretically derived by Müller at al.[9] However, the metal complex-mediated ATRP is in many ways a complex reaction (Scheme 1b)[28−30] and the authors point out that the rate constants should be regarded as apparent ones. At 100% vinyl group conversion and equal rate constants a polymer with 23.3% T and D units, 40.0% $\mathrm{L_c}$ units, and 13.5% $\mathrm{L_v}$ units should be formed having a $\mathrm{DB_{Frey}}$ of 46.6%.

Although the calculated $\mathrm{DB_{Frey}}$s ranging from 45% to 49% for all samples, except **1b**, are in good agreement with this theoretical value, a detailed inspection of the subunit contents clearly reveals deviations from the theory and exposes the limits of this structure parameter in describing a structure with different types of linear units. Samples **1c** and **1d** were obtained using the classic reaction conditions,[15] i.e., using chlorobenzene as solvent and bipyridine/CuCl as activator. The reactions were carried out at 115 °C to avoid significant HCl elimination which occurs at higher polymerization temperatures.[15] Both samples obtained with different catalyst content are of relatively high molecular-weight and do not differ significantly in the content of subunits. However, compared with the calculated values, a trend to lower $\mathrm{L_C}$ and higher $\mathrm{L_V}$ content is obvious. According to the general mechanism of ATRP (Scheme 1b) two activation/deactivation equilibria have to be considered: first that one of the chloromethyl group (**B***) and second that one of the chloromethylene group (**A***). Consequently, the propagation and also termination reactions occur by primary radicals (from **B***) and secondary radicals (from **A***). Obviously, several parameters can influence the final polymer structure and a conclusive explanation of the observed fractions of subunits seems to be impossible. We rationalize the increased $\mathrm{L_V}$ content with both a retarded deactivation and a higher reactivity of the secondary radical compared with the primary one.[31−33] Furthermore, it was reported that Cl-based systems have slow deactivation rates leading to higher polydispersity.[34] With increasing lifetime monomer addition to the chain end can occur several times. Repeated monomer addition to the secondary radical always results in $\mathrm{L_V}$ subunits, but also starting from a primary radical multiple monomer addition results in $\mathrm{L_V}$-rich sequences because the first vinyl group addition to the primary radical generates a secondary radical. Finally, the $\mathrm{L_V}$ content increases faster than the $\mathrm{L_C}$ content and the sum of all linear units is increased, too. A similar effect is observed for polymers prepared with the activators generated by electron transfer (AGET) ATRP method and lower CuCl content (**1e**−**1g**), which have a composition similar to samples **1c** and **1d**. Here, the total reaction rate seems to be lower because after comparatively or longer reaction time polymers with lower molecular weights were isolated. This is related to a lower monomer conversion explaining the more balanced ratio of $\mathrm{L_V}$ and $\mathrm{L_C}$ units for **1e** and **1f** compared to products with higher molecular weight.[9] The content of $\mathrm{L_V}$ and $\mathrm{L_C}$ units is significantly different for samples **1a** and **1b** which had been used to assign the NMR signals. Bulk polymerization of 4-CMS with bipyridine/CuCl as catalyst results in sample **1a** which is unexpectedly rich in $\mathrm{L_V}$ units. We assume that due to the high monomer concentration more monomers add to the radical species before deactivation. Contrary, **1b** is with 49% very rich in $\mathrm{L_C}$ units indicating preferred radical formation from **B***. For the synthesis of this polymer tris[(2-pyridyl)-methyl]amine (TPMA) was used instead of 2,2′-bipyridyl (bpy) as ligand in the copper complex. Compared to Cu/bpy complexes ATRP mediated by Cu/TPMA complexes is better controlled[28] which indicates a general shift of the equilibrium to the dormant species. This seems to suppress the preferred formation of $\mathrm{L_V}$ units and gives a higher chance for the formation of primary radicals leading to $\mathrm{L_C}$ units.

Considering the content of terminal and dendritic units there is a general deviation from the theoretical calculations both for equal or nonequal rate constants:[9] in each case, the content of terminal and dendritic units should be equal. Except **1a**, the determined content of T units is significantly lower than the D content and lower than the theoretical value for equal reaction rates. Here, one has to keep in mind that the samples are precipitated from the reaction solution and low-molecular-weight fractions containing a larger amount of T units are not included.

The reactivity ratio r_{theo} of the reactions **A*** + **A** (= k_A) and **B*** + **A** (= k_B) was estimated from the content of **B*** units (***B****) at full conversion ($p_A = 1$, $M = 0$) according eq 7 which was derived for ideal SCVP conditions:[9]

$$\begin{aligned} r_{\mathrm{theo}} &= k_A/k_B = (1 - p_A - \mathbf{B^*})/(\mathbf{B^*} - \ln \mathbf{B^*} - 1) \\ &\text{with } \mathbf{B^*} = \mathrm{T} + \mathrm{L_V} + \mathrm{M} \qquad (7) \end{aligned}$$

Using the content of T and $\mathrm{L_V}$ units from Table 1 r_{theo} values of **1a** (7.4) and **1b** (0.55) qualitatively agree with the claimed enhanced and retarded reactivity of the secondary radical. Values between 0.94 and 1.81 for **1c**−**1g** correspond to equal reactivity or slightly enhanced reactivity of secondary radicals. However, it is difficult to evaluate to what extent the ideal conditions, e.g., $p_A = 1$ and no cyclization, are fulfilled.

Structure Development from a Kinetics Study. On the basis of the findings given in the preceding chapters the structure development was followed by time-dependent sample drawing from a standard polymerization reaction using a [Cu]/[4-CMS] ratio of 0.1 at 115 °C for 6 h (final polymer: sample **1c**) as a proof of principle. In contrast to the comprehensive kinetic investigations on self-condensing polymerizations of 4-CMS[15] and (meth)acrylates[6,35] the molecular weights are not scope of this NMR study. Figure 5 gives the ^{1}H NMR spectra which were analyzed as described in the Supporting Information. The reaction is characterized by a fast initial stage resulting in 55% conversion of vinyl groups **A** (p_A) and 75% of the monomer within 20 min which is followed after about 1 h by a second stage which can be satisfyingly

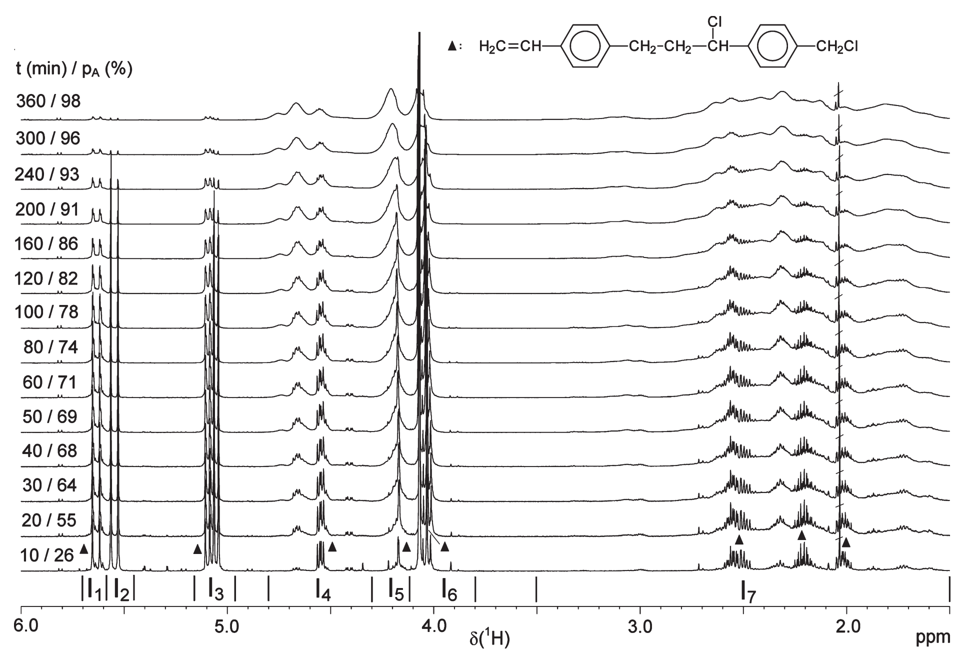


Figure 5. ^{1}H NMR spectra (region) from the kinetics experiment (solvent: C_6D_6). Reaction time and conversion of vinyl groups (p_A) are given on the left. Signals of the dimer **F-T** are marked.

described by first order kinetics characteristic for controlled radical polymerization (Figure 6a). Similarly, a fast initial period followed by a slower one was reported by Weimer et al.[15] In contrast but based on a fewer number of data points, an increasing overall polymerization rate was found in a SCVP kinetic study on the **AB*** monomer 2-((2-bromopropionyl)oxy)ethyl acrylate and explained by lowered copper(II) concentration.[6] One may argue that in the first period mainly dimers and trimers were formed as can be concluded from the NMR spectra at low conversion (Figure 5, lower traces). The monomer and the F-T dimer were proved to be the main compounds after 10 min by NMR. The dimer is present in the reaction mixture up to high conversions. Additional narrow signals indicate oligomerization. Thus, in this first stage of reaction the ratio of chloromethylene groups, which are not present in the monomer, to the chloromethyl groups changes drastically. With increasing concentration of chloromethylene groups the mechanism turns to a more controlled conversion of vinyl groups both from focal groups and monomer according to ATRP. Increasing line broadening with conversion is related to the formation of high-molecular-weight products.

The dependence of the degree of polymerization (DP) on conversion of vinyl groups (Figure 6b) is very similar to calculations of Müller et al.[8] and He and Tang.[12] This significant increase in molar mass only at high vinyl group conversion is more typical for a cluster growth (step growth) than for a chain growth process having similarities with the process of gel formation as outlined in[8]. The relatively large polydispersity which increases with the degree of polymerization (Table 1) is characteristic for highly branched polymers with numerous reactive groups in the macromolecule.

Figure 7 depicts the development of subunits starting with the second sample, i.e., $p_A > 0.5$. For comparison, the curves give the fractions of units calculated for equal rate constants k_A and k_B according to ref 9. Even though the experimental data and the curves show the same trend, the experimental values differ significantly from the calculated ones. The L_C fraction is decreased and the L_V fraction increased over the whole range of $0.5 < p_A < 1$. This is in accordance with the L_C and L_V fractions in polymer samples **1a** and **1c**−**1g** and explained by multiple monomer addition before deactivation, i.e. by lowered rate of the deactivation process of the formed propagation centers (Scheme 1b). Higher reactivity of the propagating groups was also found in the kinetic

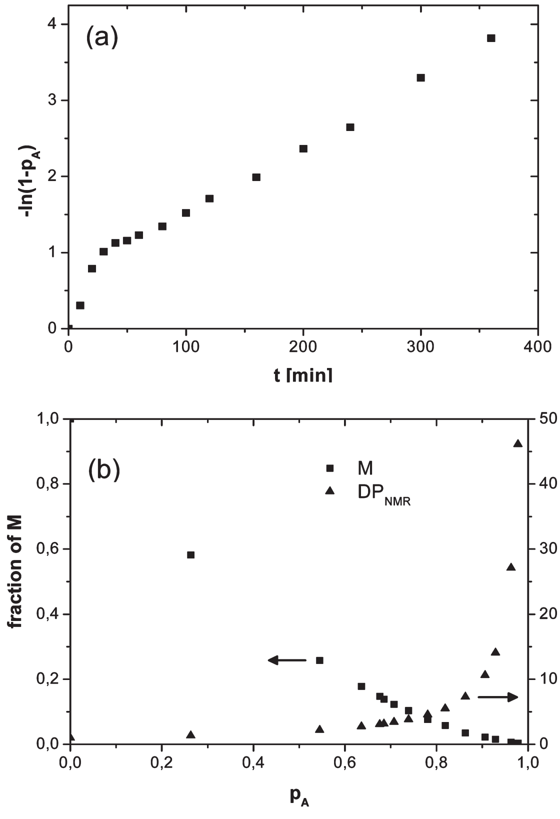


Figure 6. (a) First-order plot of conversion of vinyl groups (p_A) of monomer and focal groups as a function of reaction time and (b) monomer (M) fraction and degree of polymerization determined by NMR (DP_{NMR}; includes the monomer, i.e., $DP_{NMR} = 1$ at $p_A = 0$) as a function of p_A.

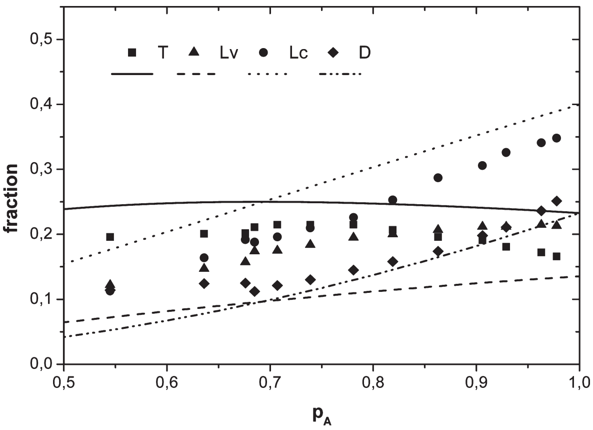


Figure 7. Fraction of T, L_V, L_C, and T units as a function of conversion p_A in the range of $0.5 < p_A < 1$. The values add to 100% with the fractions of monomer and focal unit. The lines correspond to the calculated values for equal rate constants k_A and k_B according to ref 9.

investigations on (meth)acrylates and multiple monomer addition resulting in enhanced content of vinyl-type structure was discussed.[6,35]

The kinetic curve for the T content shows a reduced content over the whole conversion range studied which indicates that the reduced T content determined for the precipitated polymers is only to some extent caused by removal of low-molecular-weight fractions. In contrast, the content of D units is slightly increased. This is a surprising finding because theoretically the content of T and D units should be equal.

One may argue that the reduced T content is caused by the proved side-reactions of the chloromethyl and chloromethylene groups under loss of chlorine and formation of, e.g., $Ar-CH_3$ groups, and by HCl elimination. This would definitely reduce the content of T and, with respect to the quantification from ^1H NMR spectra, the total intensity of signals from chlorine containing units. Furthermore, replacement of chlorine by hydrogen and biradical reactions are connected with intensity increase in the aliphatic protons region. Consequently, the content of D units would be overestimated. It is hardly possible to evaluate quantitatively these effects and also cyclization reactions but without these side reactions the polymer structure tends to result in a more balanced content of T and D units as expected from theory.

Estimating r_{theo} according to eq 7 for all conversions, the values vary within the range of 1.15 ± 0.15 indicating a slightly increased reactivity of the secondary radical. However, with several indications that ideal SCVP conditions are not fulfilled, we avoid to overinterpret the r_{theo} values calculated from the fractions of subunits.

Conclusions

In this work, we were able to prove the different characteristic structural units (terminal T, condensation-type linear L_C, vinyl-type linear L_V, dendritic D) of highly branched poly(4-chloromethylstyrene) based on careful assignment of the ^1H and ^{13}C NMR signals. The ^1H NMR spectra could be quantitatively analyzed on the level of these units combining signal integration in C_6D_6 and CD_2Cl_2 as solvents. Thus, it was for the first time possible to determine an exact value of the degree of branching for this hyperbranched polymer prepared by self-condensing vinyl polymerization.

Furthermore, the development of the structural units during the polymerization reaction was followed in a kinetics study which allowed some conclusions on possible reaction mechanisms having influence on the structure of the resulting polymer. The results have also been compared to theoretically calculated values and it was shown that similar overall degrees of branching have been achieved as predicted. However, it was also shown that the exact fractions of the various structural units cannot be predicted by a simple theoretical model as the mechanism of the atom transfer radical polymerization is way too complex. Generally, an increased content of L_V is observed for SCVP polymerization with 2,2′-bipyridyl as copper ligand. It is assumed that both a retarded deactivation and a higher reactivity of the secondary radical compared with the primary one, both resulting in multiple monomer addition before deactivation, cause the preferred formation of this unit. Although HCl elimination and formation of $Ar-CH_3$ groups could be proved a complete evaluation of the structure, especially those structures resulting from termination and side reactions, remains difficult.

Still, the results of this work should be of interest as the highly branched polymer P(4-CMS) is an interesting scaffold for further introduction of functional end groups or as an additive in polymers blends. Therefore, a detailed knowledge about its structural units, the degree of branching, and the resulting properties is of great importance.

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Supporting Information Available: Text giving the polymer syntheses, representative parameters for 2D NMR measurements, and an analysis of the ^1H NMR spectra obtained from the kinetics experiment, tables of ^1H and ^{13}C substituent chemical shifts, and figures showing additional NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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