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Universal Polymer Analysis by ^{1}H NMR Using Complementary Trimethylsilyl End Groups

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Abstract: New degenerative chain transfer agents, namely 4-(trimethylsilyl)benzyl 4′-(trimethylsilyl)butanedithioate, 4-(trimethylsilyl)benzyl 3′-(trimethylsilyl)propyl trithiocarbonate and their 3-(trimethylsilyl)benzyl isomers, that are two-fold labeled with complementary trimethylsilyl (TMS) markers, were designed and shown to be powerful tools for universal polymer analysis by conventional ^{1}H NMR spectroscopy. Their use in controlled free radical polymerization, here the reversible addition−fragmentation chain transfer (RAFT) method, resulted in polymers with low polydispersities up to high molar masses, as well as with defined complementary TMS end groups. Thus, routine ^{1}H NMR spectra allowed facile determination of the molar masses of polymers of various chemical structures up to at least 10^5 g/mol, and simultaneously provided crucial information about the content of end groups that is typically >95% when polymerizations are correctly performed. Polymerizations were carried out in various solvents for two standard monomers, namely *n*-butyl acrylate and styrene, as well as for two specialty monomers, so-called inimers, namely 2-(2-chloropropionyloxy)ethyl acrylate and 2-(2-chloropropionyloxy)ethyl acrylamide. The complementary end group markers revealed marked differences in the suitability of commonly used solvents for RAFT polymerization. The results demonstrate—beyond good polymerization control—that the new RAFT agents are universal, powerful tools for facile polymer analysis by routine ^{1}H NMR spectroscopy, of their absolute molar masses as well as of the content of end groups. This is crucial information, e.g., for the synthesis of high-quality telechelics and, in particular, of block copolymers, which is difficult to obtain by other methods. Preliminary screening experiments indicate that similar uses can be envisaged for analogous ATRP systems.

Introduction

Controlled free radical polymerization (CRP),[1−3] in particular the methods of atom transfer radical polymerization (ATRP),[4,5] nitroxyl-mediated polymerization (NMP),[6] and reversible addition−fragmentation chain transfer polymerization (RAFT),[7,8] have emerged during the past decade as potent methods to tailor polymers. Key to each of these processes are specially designed mediators which (i) reversibly terminate the active end of the growing chain and (ii) may confer specific functionalities to the polymer chain ends. Major applications of CRP are therefore the synthesis of telechelics[9−15] and, in particular, of block copolymers[3,16] from a wide range of (functional) monomers without the need of protecting groups. At the heart of all CRP methods for block polymer syntheses are polymeric intermediates, which carry the active moiety of the CRP agent and thus allow the addition of the subsequent block. Accordingly, the determination not only of the molar mass but also of the content of end groups is important for the successful synthesis of high-quality block copolymers by sequential CRP techniques. However, this information requires mostly the use of heavy and expensive specialized equipment as well as of cumbersome and time-consuming analytical procedures. This is particularly true

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when monomers bearing functional groups are used and other than linear homopolymers are to be analyzed. Mostly, therefore, only apparent molar masses and polydispersities are determined by size exclusion chromatography using standard polymers—such as polystyrene or poly(methylmethacrylate)—for calibration. In contrast, the true molar masses and, especially, the degrees of end group functionality are only assumed to be appropriate on the basis of indirect observations, due to the lack of convenient analytical tools.

A priori, end group analysis is a universal method to determine molar masses of homo- as well as copolymers. Importantly, end group analysis is also valid in the case of associating polymers, for which most other methods fail. The use of this method requires only that the average number of end groups per macromolecule is known and that the end groups can be reliably identified and quantified. In practice however, both conditions are normally difficult to fulfill. The situation is different for polymers made by living polymerizations or CRP, as all macromolecules should in very good approximation bear either exactly one or exactly two defined end groups, when using a monofunctional initiator. In the case of the thiocarbonyl-based RAFT process, the situation is particularly advantageous. The moderating RAFT agent that can be conveniently presented as R−S−C(=S)−Z, will confer one defined initiating end group R and one defined terminating end group Z to each polymer if the polymerization is conducted correctly.[17] Experimentally, the number-average molar mass M_n can then be calculated via end group analysis as

$$M_n^{exp} = M_{monomer} \times [CRU]/[R^{inc}] + M_{CTA} \quad (1a)$$

or

$$M_n^{exp} = M_{monomer} \times [CRU]/[Z^{inc}] + M_{CTA} \quad (1b)$$

with $M_{monomer}$ and M_{CTA} being the molar masses of the monomer and the RAFT chain transfer agent, respectively, and [CRU], [R^{inc}], and [Z^{inc}] being the concentrations of the constitutional repeat units (CRUs), the R-groups, and the Z-groups incorporated in the polymers, respectively. Equation 1a is based on the conditions (1) that the amount of initiator-derived polymer chains is much smaller than the ones initiated by R residues and (2) that uncontrolled chain transfer to the solvent, the monomer, and impurities is negligible. Both conditions can be fulfilled by the appropriate choice of the engaged amounts of initiator vs RAFT agent,[8,17] and of the solvent. In eq 1b, one must further assume that the extent of all reactions inducing a loss of thiocarbonyl moieties is negligible, too. This assumption is less reliable, as several side reactions of thiocarbonates and trithiocarbonates under RAFT conditions and workup are known.[18−24] Therefore, end group analysis of the molar mass should preferentially make use of the R rather than of the Z-end group. Importantly, if both end groups R and Z can be quantified independently, the degree of the end group functionality can be deduced from the ratio [Z^{inc}]/[R^{inc}].[24,25]

Several methods for end group analysis and molar mass determination of RAFT-made polymers have been applied, such as UV absorption,[20,21,26−32] SEC with UV detection,[19,33] elemental analysis,[24,30] as well as ^{1}H NMR spectroscopy.[15,24,25,30,34−45] Among these, UV absorption and ^{1}H NMR spectroscopy are preferable, as they ask only for standard equipment, and their signals provide easily quantitative information. Especially NMR analysis is attractive due to its easy accessibility and the relatively short measurement times. Still, sufficiently intense end group signals that are not obscured by signals from any other groups are required. Hence, compounds which are effective CRP agents and, in addition, exhibit intense NMR signals in a spectral region free of interferences by common solvents and polymers are desirable. For the sake of best signal-to-noise ratios, singlet signals are preferred. So far, several examples for end group analysis *via* ^{1}H NMR spectroscopy have been reported. However, the RAFT agents used typically had only NMR marker groups, which showed up in the range of 0.8−8 ppm, i.e. in the range where many polymers show signals of

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their CRUs and which give broad and low intensity signals. Hence, the NMR markers introduced by the RAFT agents have been typically useful for particular cases only, often allowing only the quantification of either the Z[36,38−40,46] or—even more seldom —of the R group,[45,47,48] and were relatively imprecise for M_n values above 10,000.

An outstanding example for a NMR label is the trimethylsilyl (TMS) group, as it (i) can be conveniently introduced, (ii) is sufficiently stable when attached to carbon, and (iii) has nine equivalent protons giving rise to an intense singlet signal in a spectral region that is usually NMR silent (0−0.5 ppm). Moreover, the proton signals of TMS groups attached to alkyl residues appear at 0.00−0.05 ppm, whereas signals of aryl-bound TMS groups are typically found between 0.2 and 0.4 ppm. The observed deshielding of protons in aryl-bound TMS groups can be accounted for by ring current effects.[49,50] Therefore, TMS groups on both R- and Z-group may display two separated singlets and, thus, provide information about molar mass and end group functionality simultaneously. This seems most useful inasmuch as losses of Z-groups during synthesis and workup can occur and may be quantified conveniently by comparing the signals of the R- and Z-groups (*vide infra*).

Herein, we report on the synthesis of four novel, doubly TMS-labeled RAFT agents as well as their use in polymerizations of two standard monomers, namely *n*-butyl acrylate and styrene, and of two specialty monomers, so-called inimers (initiator-monomer) as used e.g. for self-condensing vinyl polymerization,[51−54] or molecular brushes,[55−58] namely the inimers 2-(2-chloropropionyloxy)ethyl acrylate and 2-(2-chloropropionyloxy)ethyl acrylamide, in various solvents. Dithioesters as well as trithiocarbonates with an aromatic R-group, substituted with a TMS-label in the 3- and 4-position, and an aliphatic Z-group, containing a terminal TMS-label, were prepared, which proved to be suitable for the controlled polymerization of polymers with a molar mass of up to 10^5 g/mol. Moreover, the TMS_R- and TMS_Z-resonances provided information about the molar mass as well as the content of end groups from routine ^{1}H NMR spectra. This allowed the identification of unexpected side reactions, which otherwise would have been hard to detect, let alone to analyze and to avoid by adapting the polymerization procedures.

Experimental Section

The methods and chemicals used are specified in the Supporting Information. 4-(Trimethylsilyl)benzyl bromide (**4-TBzB**) and 3-(trimethylsilyl)benzyl bromide (**3-TBzB**),[59,60] 3-trimethylsilyl-1-propanethiol,[61] as well as 2-(2-chloropropionyloxy)ethyl acrylate (**ClPEA**)[57] were synthesized according to published procedures. 2-(2-Chloropropionyloxy)ethyl acrylamide (**ClPEAm**) was prepared in two steps from acryloylchloride, ethanol amine, and 2-chloropropionic acid chloride. RAFT agents 4-(trimethylsilyl)benzyl 4′-(trimethylsilyl)butane-dithioate (**1**) and 3-(trimethylsilyl)benzyl 4′-(trimethylsilyl)butane-dithioate (**2**) were synthesized by addition of CS_2 to the Grignard derivative of 3-chloropropyltrimethylsilane and subsequent *S*-alkylation by the corresponding trimethylsilyl-benzylbromides. The analogous synthesis of 4-(trimethylsilyl)benzyl 3′-(trimethylsilyl)propyl trithiocarbonate (**3**) and 3-(trimethylsilyl)-benzyl 3′-(trimethylsilyl)propyl trithiocarbonate (**4**) started from 3-(trimethylsilyl)-1-propanthiol. The synthetic procedures for the new compounds and their analytical data are specified in the Supporting Information, as are the detailed conditions for the polymerization reactions.

Results and Discussion

Design of the RAFT Agents. Numerous types of RAFT agents have been prepared and tested in polymerization reactions.[8,17,62] Common choices for the R- and the Z-group are benzyl and alkyl, aryl or *S*-alkyl groups, respectively. RAFT agents with a benzyl or aryl moiety, for instance, may be used to evaluate the molar mass for poly(alkyl(meth)acrylate)s,[30,34−36,63] poly(alkyl-(meth)acrylamide)s[25,26,39,44] or poly(acrylonitrile)[38] by ^{1}H NMR since there is no spectral overlap of the end group and the polymer signals. Still, for high molar mass polymers one aromatic end group is generally not suitable for end group analysis due to the complex signal pattern and to the low intensity of the useful signals of the aromatic protons. Also, in most reports on end group analysis *via* ^{1}H NMR, only one end group, mostly the less reliable Z-group, has been used. In any case, when using polymers with aromatic moieties in the CRUs, such as styrene and its derivatives, the overlap of the end group and polymer signals prevents generally molar mass determination by NMR spectroscopy. Obviously, these limitations become even more severe in the case of copolymers, due to the higher diversity of NMR signals that may superpose a possible end group signal.

In order to overcome this limitation and to develop generally applicable RAFT agents for facile end group analysis *via* ^{1}H NMR, we designed RAFT agents that are labeled at both the R- and the Z-group with TMS markers. These give rise to two singlet signals in a spectral region that is usually NMR silent (namely, 0−0.5 ppm). The chemical structures of the new RAFT agents are shown in Figure 1. The reinitiating benzylic R-groups, being TMS-labeled on the aryl residue in the 3- or 4-positions, are connected to the alkyl-bound TMS in the Z-group *via* either a dithiocarboxylate or a trithiocarbonate moiety. The propyl

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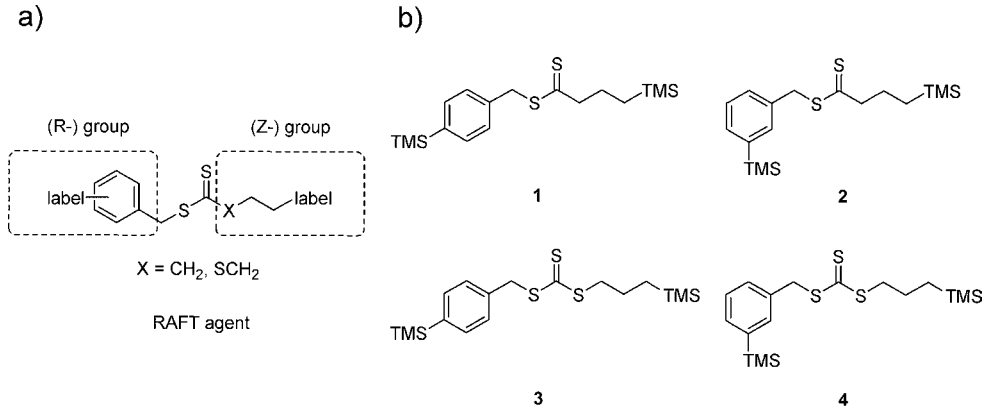

Figure 1. (a) General structure of RAFT agents used; (b) structure of the two-fold TMS-labeled RAFT agents synthesized.

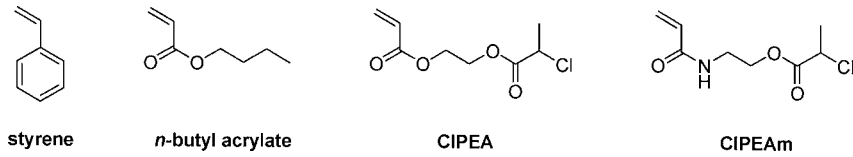

Figure 2. Chemical structure of the monomers investigated.

spacer between the aliphatic TMS residue and the thiocarbonyl moieties was chosen because exploring studies with a shorter spacer group to produce benzyl 2-(trimethylsilyl)ethanedithioate indicated important side reactions involving the TMS group (cf. Supporting Information). The RAFT agents were thus synthesized starting from 3-chloropropyltrimethylsilane for **1** and **2**, and from trimethylallylsilane for **3** and **4**. The TMS-free analogous dithioesters[64−66] and trithiocarbonates[58,67,68] have already been used successfully in RAFT polymerizations of styrenic and acrylic monomers, suggesting the effectiveness of **1**−**4** in RAFT polymerizations.

To demonstrate the usefulness of the end group labeling with the new RAFT agents, a series of styrenic, acrylate, and acrylamide monomers were studied (Figure 2). First, polymerizations were performed on styrene (**St**) and *n*-butyl acrylate (**BuA**), as these standard polymers can be easily analyzed by SEC calibrated by appropriate standards to give correct absolute molar mass values. Indeed, the Mark−Houwink−Sakurada parameters of **poly(St)** and **poly(BuA)** are virtually identical in THF, so that calibration by **poly(St)** standards provides also true molar masses for **poly(BuA)**.[69,70] Subsequently, two specialty monomers ("inimers"), namely the acrylate **ClPEA** and the acrylamide **ClPEAm** were polymerized and analyzed. While the synthesis of **ClPEA** was described before,[57,58] **ClPEAm** was newly synthesized.

Polymerization of *n*-Butyl Acrylate (BuA). First, **CTA1** was used for RAFT polymerization of **BuA** in THF, benzene, and ethyl acetate. The results are given in Table 1 (entries 1−10). For all the RAFT agents **1**−**4**, polymerization of BuA in benzene or ethyl acetate provided **poly(BuA)** with monomodal molar mass distributions and relatively low polydispersities of about 1.1−1.2 (Table 1, entries 3−10), strongly suggesting good control over the polymerization process. The number average molar mass values M_n, which were calculated theoretically and which were measured by SEC, agreed well, as did the M_n values determined by ^{1}H NMR end group analysis using either the TMS_R or the TMS_Z label (see Figure 3). From their relative intensity ratios, it is seen that Z/R is close to unity (Table 1). Thus, the RAFT end groups are very well preserved. Therefore, the polymers made have not only a very high end group functionality, if aimed at uses as telechelics, but may serve also as high quality macro RAFT agents for preparing block copolymers (*vide infra*).

In order to learn about the limits of molar mass determination by ^{1}H NMR, $\mathbf{poly(BuA)_{580}}$ was synthesized (Table 1, entry 7). Even in this case, the TMS signals were sufficiently intense to allow the convenient determination of M_n (Figure 3b) The values determined *via* the TMS_R as well as *via* the TMS_Z signals agreed very well with both the theoretically expected one and the SEC result, demonstrating that the TMS-labeled RAFT agents are indeed powerful tools to determine molar masses of at least up to 10^5 g/mol with good precision. Moreover, the comparison of the results obtained from both labels allows a fast and efficient check for preservation of the RAFT end groups. This is a most precious, but nontrivial, information that is otherwise extremely difficult to obtain.

In THF, polymerization provided $\mathbf{poly(BuA)_{41}}$ and $\mathbf{poly(BuA)_{191}}$ with monomodal molar mass distributions, too, but with somewhat larger polydispersities of 1.6 and 1.3, respectively (Table 1, entries 1 and 2) than in benzene or ethylacetate. The simultaneous labeling of the R- and Z-end groups by the complementary TMS groups enabled us to determine the Z/R ratio of $\mathbf{poly(BuA)_{191}}$ to be only 0.80, thus indicating a ∼20% loss of CTA functionality during the polymerization. This partial loss of the dithioester groups implies that a subsequent block

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Table 1. RAFT Polymerization of Styrene (**St**) and *n*-Butyl Acrylate (**BuA**) at 65 °C, Initiated by AIBN, and Characterization of the Polymers **poly(St)** and **poly(BuA)**[a]

							SEC[c]		end group analysis		
entry	monomer	CTA	solvent	*t* [h]	%[b]	M_n^{theor}	M_n	PDI	M_n[d]	DP_n[d]	Z/R
1	BuA	**1**	THF	0.5	18	5000	4300	1.62	5700	41	0.98
2	BuA	**1**	THF	2	78	20300	17500	1.30	25000	192	0.80
3	BuA	**1**	benzene	2	73	18700	23000	1.13	21800	167	0.99
4	BuA	**1**	benzene	4	89	23100	28500	1.16	26500	206	0.93
5	BuA	**1**	EtAc	2	68	17400	22800	1.12	20000	153	0.99
6	BuA	**1**	EtAc	4	93	24200	26200	1.15	25400	195	0.97
7	BuA	**1**[b]	EtAc	9	56	72300	66500	1.17	74600	580	0.98
8	BuA	**2**	EtAc	2	53	14000	16900	1.13	15400	117	0.99
9	BuA	**3**	EtAc	2	66	17300	20400	1.13	19500	150	0.98
10	BuA	**4**	EtAc	2	51	13400	16000	1.14	15000	114	0.99
11	St	**1**	bulk	12	30	6100	6600	1.41	7600	69	0.99
12	St	**2**	bulk	12	30	6100	6700	1.46	7800	72	0.99
13	St	**3**	bulk	12	32	7100	6400	1.45	8300	76	0.99
14	St	**4**	bulk	12	32	7100	7300	1.47	8500	78	0.98
15	St	**1**	bulk	22.5	60	11500	11800	1.23	11900	110	0.97
16	St	**1**[e]	bulk	69	79	74100	61200	1.22	77600	743	0.94
17	St	**2**	bulk	22.5	68	13400	14200	1.22	14800	139	0.98
18	St	**3**	bulk	22.5	70	15100	14200	1.21	15700	147	0.99
19	St	**4**	bulk	22.5	75	16200	15600	1.20	16800	157	0.98
20	BuA	**poly(St)$_{147}$**	EtAc	16	92	39300	36000	1.21	41000	192	0.94

[a] Polymerization conditions: [monomer]/[CTA]/[AIBN] = 200:1:0.1. [b] Conversion determined by ^{1}H NMR analysis of the crude product. [c] RI detection, calibrated using polystyrene standards. [d] By ^{1}H NMR, using the intensity of the TMS_R signal. [e] Modified polymerization conditions: [monomer]/[CTA]/ [AIBN] = 1000:1:0.1.

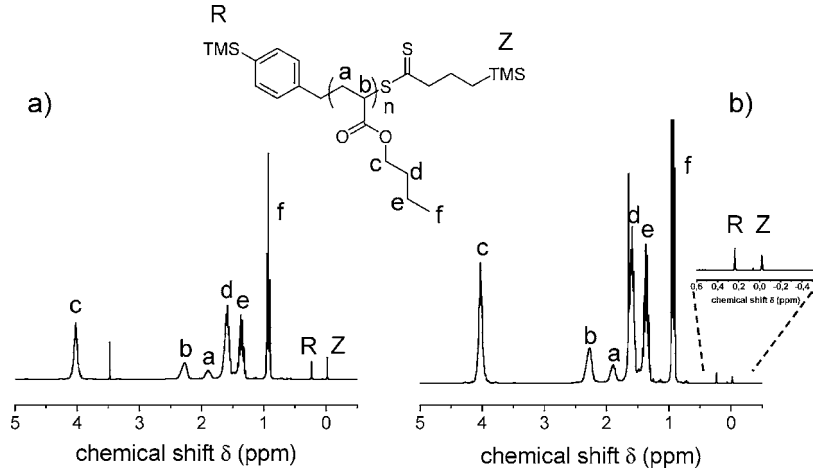

Figure 3. ^{1}H NMR spectra of **poly(BuA)$_{153}$** (a) and **poly(BuA)$_{580}$** (b) in $CDCl_3$.

copolymerization would provide a mixture of diblock copolymer and dead homopolymer, which are generally difficult to separate from each other. Therefore, it seems advisible to avoid THF as solvent in the RAFT process, if very high-quality polymers are required. These results agree with the findings of a recent degradation study of RAFT end groups in THF.[23] In the latter study, a radical degradation mechanism due to hydroperoxides was proposed. Keeping in mind that we distilled the THF freshly from NaK/benzophenone prior to polymerization and worked under inert gas all the time, one may think about alternative explanations for the observed loss of end groups (which, however, is beyond the scope of this work). In any case, it seems that THF, although appearing convenient by virtue of its good dissolving power for many polymers, is not the solvent of first choice to prepare high-quality block copolymers by the RAFT process.

Polymerization of Styrene. Whereas benzylic R-groups are rarely suitable for the end group analysis of polystyrene and its derivatives due to the spectral overlap of end group and polymer signals, RAFT agents **1**−**4** worked perfectly for the thermally initiated polymerization of styrene and subsequent analysis of the polymers by ^{1}H NMR spectroscopy (Figure 4). All RAFT polymerizations provided **poly(St)** with monomodal mass distributions and relatively low polydispersities of 1.2−1.5. The molar masses determined by integrating the ^{1}H NMR signals of both TMS labels of the R- and the Z-groups were in good agreement with both the theoretically expected M_n values and the molar masses measured by SEC analysis calibrated with polystyrene standards (Table 1, entries 11−19). The comparison of the intensities of the TMS_R and TMS_Z groups indicated again ratios of Z/R close to unity, i.e. excellent preservation of the RAFT end groups. Even the molar mass of **poly(St)$_{743}$** of about 70,000 could still be determined conveniently. Hence, as for **poly(BuA)**, TMS-labeled RAFT agents are powerful tools for a convenient molar mass determination of polystyrenes, too.

However, in contrast to **poly(BuA)**, the ^{1}H NMR signals of both TMS labels in the **poly(St)** samples did not show defined singlets but were—to our surprise—split into complex signal groups each (Figure 5a−d). Similar findings were reported for

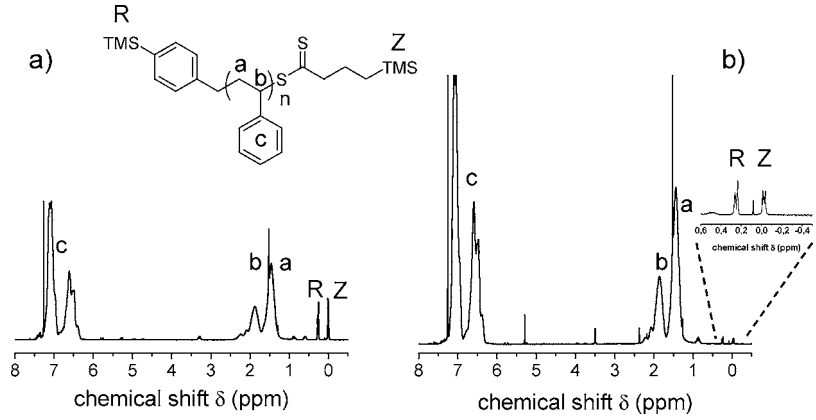

Figure 4. ^{1}H NMR spectra of **poly(PS)$_{110}$** (a) and **poly(PS)$_{743}$** (b) in $CDCl_3$.

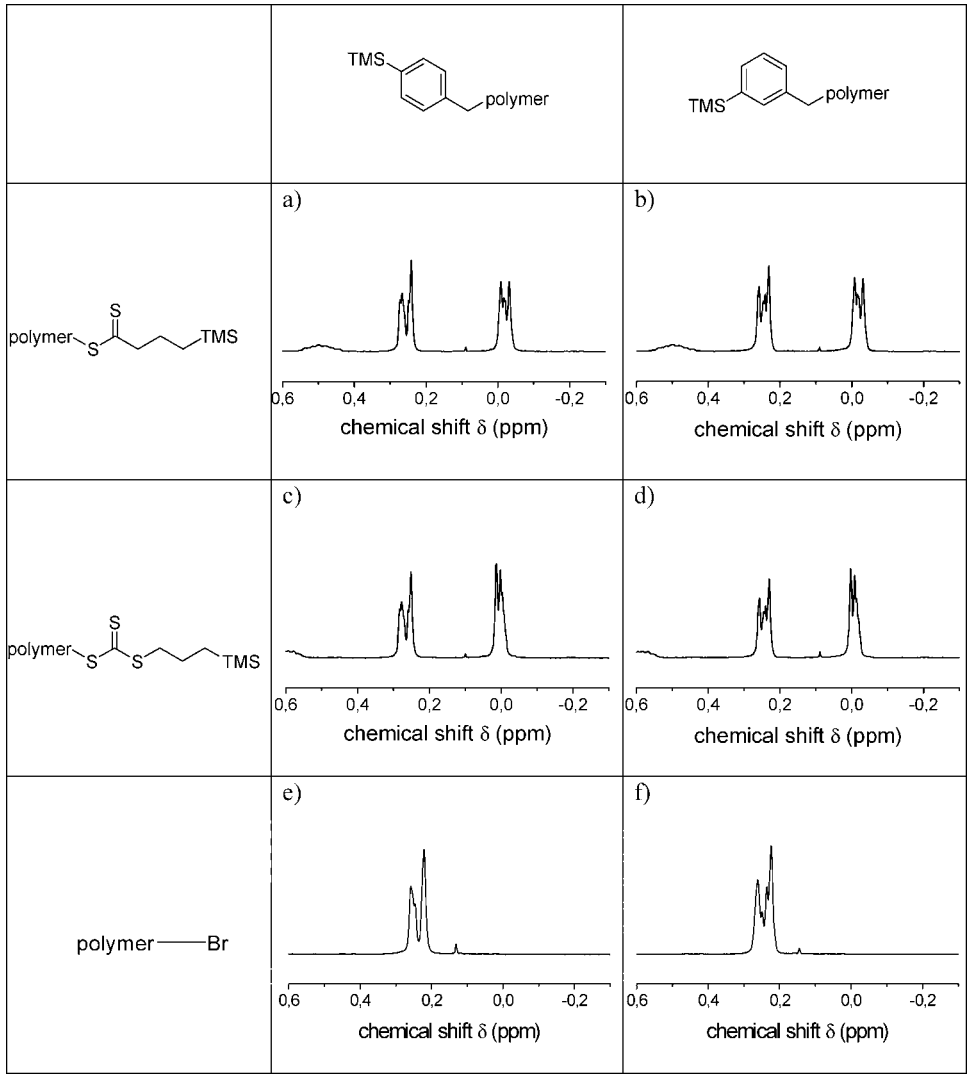

Figure 5. Comparison of the ^{1}H NMR signals of the TMS end group labels of **poly(St)** samples made with RAFT agents (a) **1**, (b) **2**, (c) **3**, and (d) **4**, or by ATRP using for initiation (e) 4-(trimethylsilyl)benzyl bromide and (f) 3-(trimethylsilyl)benzyl bromide, respectively.

TMS-terminated oligomeric styrene chains before[71] a detailed NMR study revealing that the complex signal groups arose from stereo isomerism, i.e. from CRU sequences with different tacticities at the chain ends. Noteworthy, while the TMS end groups in the latter report were directly placed at the polymer chain end, in our systems the TMS groups are separated by nine bonds from the first stereo center in the polymer backbone. This indicates that the peak splitting is a combined effect of stereoisomerism with the anisotropy effects of the adjacent aromatic rings.[49,50]

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Table 2. Bulk Polymerization of Styrene (**St**) by ATRP at 110 °C, and Analytical Data of the **poly(St)** obtained[a]

					SEC[c]		end group analysis		
entry	initiator	*t* [h]	%[b]	M_n^{theor}	M_n	PDI	M_n[d]	DP[d]	Z/R[e]
1	4-TBzB	1	38	4200	3600	1.09	3600	35	1.0
2	4-TBzB	2	55	6000	5400	1.11	5200	50	0.8
3	4-TBzB	3	64	6900	6300	1.11	6300	60	0.9
4	3-TBzB	1	36	4000	3300	1.12	3300	32	0.9
5	3-TBzB	2	54	5900	5600	1.14	5400	52	0.9
6	3-TBzB	3	65	7000	7000	1.12	6700	64	0.8

[a] Polymerization conditions: [monomer]/[initiator]/[CuBr]/[dNbpy] = 100:1:1:2. [b] Conversion determined by ^{1}H NMR analysis of the crude product. [c] Calibrated using polystyrene standards. [d] By ^{1}H NMR, using the intensity of the TMS_R signal. [e] by ^{1}H NMR, based on the relative the intensities of the TMS_R signal and of the >CHBr end group signal at about 4.6 ppm.

Indeed, a closer comparison of the spectra of the **poly(St)** samples made with the four RAFT agents **1**−**4** revealed that the R- and the Z-group split systematically (Figure 5). While the TMS_Z signals were virtually identical for all polymers bearing a given Z group (Figure 5a−b and 5c−d), the splitting of TMS_R signals depended on the substitution pattern of the trimethylsilylbenzyl group, i.e., the TMS-label in 3- and 4-position led to different peak patterns (cf. Figure 5a and c with Figure 5b and d). Although sensitivity and precision of the TMS group integrals inevitably suffer somewhat for higher molar masses due to the signal splitting (in comparison to the analysis of **poly(BuA)**), the TMS signals were still useful to determine the molar mass of the polymers as shown by comparison with SEC results (Table 1). Also, the analysis of the R/Z ratio was still possible.

The explanation for the splitting of the TMS signals was corroborated by a chain extension experiment. The preparation of **poly(St)**−***b***−**poly(BuA)** using **poly(St)$_{147}$** (Table 1, entry 18) as macro-RAFT agent (Table 1, entry 20) gave a well-defined singlet for the TMS_Z signal at about 0 ppm, while the complex pattern of the aryl bound TMS_R signal at about 0.25 ppm was retained. Due to the separation of the Z-end group from the **poly(St)** block by the added **poly(BuA)** block, the TMS_Z group is no more influenced by adjacent phenyl rings, whereas inherently, the situation has not changed for the TMS_R group.

Importantly, the monomodal mass distribution as well as the relatively low polydispersity of the block copolymer indicated good polymerization control and efficiency of the macro-RAFT agent for chain extension. Moreover, even in the block copolymer the resolved NMR-signals enabled us to verify the M_n values directly by end group analysis, and to establish the ratio R/Z being well above 90% yet (Table 1, entry 20). Inevitably, the R/Z ratio of 0.94 is somewhat lower for the chain extended polymer than for the macro RAFT agent employed (Z/R = 0.99) due to a certain number of chain termination reactions occurring. Still, these analytical data reveal that the diblock copolymer made would be perfectly suited as a high quality macro RAFT agent for a subsequent additional chain extension reaction of a third block. Commonly in the past, molar masses of such block copolymers made by CRP methods were mostly determined only indirectly. The average comonomer composition of the block copolymer is analyzed *via* ^{1}H NMR spectra, and the molar mass is calculated with the assumption that the M_n value of the first block has been fully preserved. Also, the extent of active end groups for the chain extension has been mostly not known. Obviously, the situation is much more advantageous when using RAFT agents **1**−**4** due to the two-fold TMS labels.

To rule out any peculiar effects of the RAFT process on the end group signals, 3-(trimethylsilyl)benzylbromide (**3-TBzB**) and 4-(trimethylsilyl)benzylbromide (**4-TBzB**) were employed to initiate the ATRP polymerization of styrene (Table 2). Again, the TMS signals of the initiator derived end groups in the **poly(St)** samples thus prepared exhibited the same peak splitting (Figure 5e,f) as observed in the RAFT polymerization when using agents **1**−**4**.

Also, the M_n values derived from NMR end group analysis were in good agreement with the SEC results, and polydispersities were relatively low (1.1−1.2). Importantly, preliminary ATRP polymerization experiments of acrylate using initiator **4-TBzB** resulted in polymers exhibiting a well-defined singlet signal for the TMS label, as observed when polymerizing **BuA** in the presence of RAFT agents **1**−**4**. All these findings corroborate the explanation of the observed splitting of the end group signals in the case of **poly(St)**. Noteworthy, the **poly(St)** samples made *via* ATRP contain inherently a −CH(Aryl)−Br group at the active end of the polymer chain. This group gives rise to a distinct ^{1}H NMR signal at about 4.6 ppm and therefore can also provide information about the relative amounts of initiating and terminating end groups in the polymers (Table 2). However, this signal is in a spectral region that is more prone to be superposed by signals of the polymer chain and is inevitably broad and weak. Therefore, it is difficult to quantify reliably, in particular for molar masses above 10,000. Accordingly, the use of a TMS end group marker is also helpful for molar mass analysis when applying ATRP, but is more limited in the informations provided, in comparison to the case for RAFT. In the case of third major CRP method, namely of NMP polymerization, however, one may envisage the use of analogously substituted alkoxamine initiators, with complementary TMS markers located on the N- and O-substituents, respectively, for molar mass analysis as exemplified for RAFT polymerization in this study.

Polymerization of ClPEA and ClPEAm. In order to demonstrate the general utility of the new TMS-labeled RAFT agents for determining molar masses conveniently *via* ^{1}H NMR analysis, we chose **1** in a second phase to investigate the RAFT polymerization of two unconventional monomers, so-called inimers, namely of acrylate **ClPEA** and acrylamide **ClPEAm**, for which appropriate polymer standards for SEC calibration do not exist. The polymerization of such monomers gives rise to densely functionalized reactive polymer backbones, which afford the preparation of molecular brushes *via* "grafting from" processes.[72,73]

The results of the polymerization of both **ClPEA** and **ClPEAm** are listed in Table 3. Initially, the inimer **ClPEA** was

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Table 3. Synthesis and Characterization of **poly(ClPEA)** and **poly(ClPEAm)** by RAFT Polymerization at 65 °C, Initiated by AIBN[a]

							SEC		end group analysis		
entry	monomer	CTA	solvent	*t* [h]	%[b]	M_n^{theor}	M_n^{app}	PDI	M_n[c]	DP[c]	Z/R
1	ClPEA	**1**	THF	2	56	23000	4900[d]	1.67	30000	112	0.48
2	ClPEA	**1**	THF	15	96	39000	3400[d]	1.79	47000	192	0
3	ClPEA	**1**	C_6H_6	12	69	29000	19000[d]	1.22	31000	151	0.90
4	ClPEA	**1**	EtAc	8	25	10000	7000[d]	1.38	10000	47	0.93
5	ClPEAm	**1**	THF	2	77	31000	17000[e]	1.17	37000	154	0.40
6	ClPEAm	**1**	EtAc	13	86	36000	25000[e]	1.12	33000	159	0.93

[a] Polymerization conditions: [monomer]/[CTA]/[AIBN] = 200:1:0.1. [b] Conversion determined by ^{1}H NMR analysis of the crude product. [c] By ^{1}H NMR, using the intensity of the TMS_R signal. [d] SEC in THF (RI detection), based on calibration with polystyrene standards. [e] SEC in NMP (RI detection), based on calibration with polystyrene standards.

polymerized in THF, providing **poly(ClPEA)$_{112}$** and **poly(ClPEA)$_{192}$** (Table 3, entries 1−2). Comparison of the theoretically calculated molar masses M_n^{theor} with the apparent molar mass values derived from SEC analysis shows strong differences, which is a priori not surprising in the light of the calibration by polystyrene standards. The comparison of M_n^{theor} with the experimental M_n values derived from end group analysis using the TMS_R marker match much better, still, there is a 20−30% difference. In combination with the observed polydispersities of 1.6−1.8, this points to moderate control only over the polymerization process. This finding is also reflected in the low Z/R ratios. This was in the case of **poly(ClPEA)$_{112}$** about 0.5 only, indicating a massive 50% loss of chain transfer functionality. For **poly(ClPEA)$_{192}$** (Table 3, entry 2) the loss of end group functionality is even virtually complete, as the Z-group-bound TMS moiety could no more be detected in the NMR spectra. Note that, in the latter case, polymerization of **ClPEA** was conducted nearly to completion.

Similarly for the polymerization of **ClPEAm** in THF (Table 3, entry 5), the apparent molar mass values derived from SEC analysis deviate substantially from the theoretically calculated molar masses M_n^{theor}, while the latter values and experimental M_n (*via* the TMS_R marker) are relatively close. Moreover, the ratio Z/R of **poly(ClPEAm)** obtained from end group analysis indicated about 60% loss of the RAFT active groups in the polymer formed. These results clearly demonstrate the particular merit of the TMS labels for polymer analysis especially in the case of more complex monomers, as these data cannot be deduced from most other molar mass analysis methods. In particular, SEC analysis is not only blind toward such complications due to loss of active end groups but even may (wrongly) make believe that high-quality macro RAFT agents were prepared due to the low measured polydispersity of 1.2.

Different from polymerization in THF, the RAFT polymerizations in benzene or ethyl acetate provided **poly(ClPEA)** and **poly(ClPEAm)** not only with monomodal mass distribution and relatively low polydispersities of 1.1−1.2 but also with the desired high content of end groups (Table 3, entries 3, 4, and 6; see also Figures S3 and S4 [Supporting Information]). This is indicated by the Z/R ratios >0.9. Furthermore, ^{1}H NMR spectroscopy enabled us to determine easily the absolute values of M_n, whereas the molar masses measured by SEC analysis are only apparent because of the calibration by PS standards and are therefore, at best, approximate only. The experimentally determined values by end group analysis agree very well with the theoretically calculated ones, while the apparent molar masses derived from SEC analysis inevitably deviate from the true values. The good agreement of the theoretically calculated and end group analyzed experimentally determined molar masses was corroborated for the **poly(ClPEA)$_{151}$** sample by membrane osmometry in toluene. Osmometry provided a value of 35,500 for M_n, that compares very well with the value of 31,000 derived from end group analysis. These findings demonstrate that the TMS-labeled RAFT agents are well suited to control the polymerization even of complex monomers, such as inimers **ClPEA** and **ClPEAm**, and simultaneously allow characterizing them easily and efficiently.

Conclusions

Four novel two-fold labeled RAFT agents with complementary trimethylsilyl (TMS) markers on the benzylic R- and on the alkyl Z-groups were designed. They proved to be suitable chain transfer agents for the controlled radical polymerization of various standard monomers such as styrene and *n*-butyl acrylate as well as of complex monomers such as the inimer acrylate **ClPEA** and acrylamide **ClPEAm**. Moreover, the complementary TMS marker groups allowed a facile analysis of the absolute molar masses of the polymers and of their end group functionality, and this with routine ^{1}H NMR apparatus, without the need for expensive specialized equipment or for complicated and time-consuming methods. The viability of molar mass determination by routine ^{1}H NMR spectroscopy by virtue of the end group markers was validated by a comparison of these analytical data with the results SEC for standard polymers polystyrene and poly(*n*-butyl acrylate), for which appropriate calibration standards exist. Preliminary studies demonstrated that the same concept can be extended to other CRP methods, such as ATRP polymerizations, too. In addition, the relative intensities of the complementary TMS marker groups at the α- and ω-positions of the polymer chain proved a powerful tool to determine the remaining end group functionality, information that is very difficult to obtain otherwise. This enabled us to judge the suitability of various solvents for controlled RAFT polymerizations (revealing that the widely used solvent THF is not ideal) and provided a direct measure of the active polymer chain ends, which are needed, e.g., for the synthesis of block copolymers.

Finally, we note that the aryl-bound TMS groups may allow additional functionalization *via* postpolymerization modification of the end group-labeled polymers by, for instance, *ipso*-borodesilylation[74,75] or *ipso*-bromodesilylation.[76]

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Supporting Information Available: Scheme of the synthetic pathways to compounds **1**-**4**. Details on the synthesis and analytical data of all new compounds and their intermediates, as well as on model compound benzyl 2-(trimethylsilyl)-ethanedithioate, including a putative mechanism for the observed side reaction. Conditions and protocols for the polymerizations, and selected SEC elugrams of the polymers prepared. This information is available free of charge via the Internet at http://pubs.acs.org.

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