Star-Shaped Poly(tetrahydrofuran) with Reactive End Groups: Design, MALDI-TOF Study, and Solution Behavior

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ABSTRACT: Star-shaped poly(tetrahydrofuran) (PTHF) with up to six allyl end groups was prepared by living cationic ring-opening polymerization. A functional initiation system, using allyl alcohol and trifluoromethanesulfonic anhydride, was used, followed by end-capping of the living polymer chains with the multifunctional termination agent tris(2-aminoethyl)amine. In this way, star-shaped PTHF with allyl end groups could be synthesized, with varying molecular weight (6000−20 000 g·mol^{-1}) and number of arms (three to six). Subsequently, the terminal allyl functions were quantitatively transformed into hydroxy groups using a hydroboration procedure. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) analysis, NMR, and size exclusion chromatography confirmed the controlled synthesis of these reactive star-shaped structures. MALDI-TOF was successfully used to determine the absolute molecular weight and purity of star-shaped polymers. They were further characterized by viscosimetry measurements, and their properties were compared to their linear analogues. For the same molecular weight, the stars had a strong reduced viscosity in solution.

Introduction

Because of their remarkable properties, star polymers continue to attract attention in polymer research.[1,2] Star polymers have different rheological and mechanical properties and exhibit higher degrees of end group functionality compared to their linear analogues. Controlled synthesis of star polymers can also help in the investigation of structure−property relationships in polymer science. Star polymers are generally prepared in two ways. In the "arm first" approach, the star polymers are prepared by adding a multifunctional termination[3,4] agent or a bifunctional comonomer[5] to living linear polymer chains. The main problem with this approach is that separation techniques often have to be used to remove uncoupled linear polymers. The second method, the "core first" approach, is used to synthesize star polymers by growing branches from a multifunctional active core. In this way, star polymers are produced with well-defined structures in terms of the number and length of the arms. Furthermore, there is no need to remove linear polymers since the reaction product only consists of star polymers. The central core can be built upon reaction of short living chains with a bifunctional monomer, but stars with a large fluctuation of their functionalities are obtained.[6,7] For other core first approaches, the synthesis of a well-defined multifunctional initiator is required. For ionic polymerizations, these are often difficult to prepare due to the poor solubility and stability of the multiply charged complexes.[8−11] Recent developments in atom-transfer radical polymerization (ATRP) and reversible addition−fragmentation chain-transfer polymerization (RAFT) have made it possible to use radical polymerization for the controlled synthesis of star polymers. With these techniques, a variety of multifunctional initiators have been developed and successfully used.[12−19]

Although end group reactive star polymers offer interesting perspectives to a number of applications such as a novel route to nanoparticles, nanocontainers, or nanoporous layers,[20−25] only a limited amount of work has been done on the synthesis of such reactive stars. Zimmerman et al. synthesized chain-functionalized star polymers, from which nanosized "cored" star polymers could be created after removal of the multifunctional initiator.[20] Gnanou et al. described six-arm poly(ethylene oxide) (PEO) stars, carrying pyridyl, pyridinium, or hydroxyl end groups,[26] and six-arm polystyrene (PS) with allyl, hydroxyl, and hexafullerene end groups.[27] The latter can be used in the context of "smart" materials, whereas the hydroxyl functions can be used to prepare star block copolymers (e.g., star(PS-*b*-PEO)$_6$).

The purpose of this work is to broaden the possibility of synthesizing star polymers with reactive end groups by using the living cationic ring-opening polymerization (CROP) of tetrahydrofuran (THF). We previously described the functional initiation of the THF polymerization using several kinds of alcohols and trifluoromethanesulfonic anhydride (Tf$_2$O),[28−32] and the synthesis of star-shaped poly(tetrahydrofuran) (PTHF) by using a multifunctional termination agent.[33] This work combines those routes to synthesize novel allyl functionalized star polymers based on PTHF. The use of allyl end groups offers interesting perspectives since they can be used as a (co)monomer in further polymerization reactions or they can be easily transformed into other functional groups.[26,27] This will be illustrated by a quantitative transformation of the end groups into hydroxyl functions by hydroboration. The reactive star polymers were characterized by NMR and size exclusion chromatography (SEC). Furthermore, an extensive matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) spectroscopic study was performed to determine the exact structure of the stars. Finally, their solution behavior was also investigated with viscosity measurements.

Experimental Section

Materials. Tris(2-aminoethyl)amine (TAEA; Aldrich 96%) and 2,2,6,6-tetramethylpiperidine (TMP; Acros 98%) were purified by distillation from CaH$_2$ and were stored on molecular sieves (4 Å). Tetrahydrofuran (THF; Acros 99+%) was dried on sodium wire under reflux in the presence of traces of benzophenone until a blue color persisted; it was used directly after distillation. Dichlo-

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Table 1. Experimental Results for Synthesis of Star-Shaped Poly(tetrahydrofuran) with Allyl End Groups[a]

reaction code	no. of arms[b]	M_n(arm) SEC[c] (g·mol^{-1})	M_n(arm) MALDI-TOF (g·mol^{-1})	M_n(arm) ^{1}H NMR (g·mol^{-1})	PDI(arm) SEC	M_n(star) SEC[c] (g·mol^{-1})	PDI(star) SEC
A	2.8	1000	*d*	1000	1.26	1800	1.31
B	3.3	1300	*d*	1200	1.28	3400	1.28
C	2.6	2100	2000	2200	1.24	5500	1.33
D	4.1	6000	5900	6100	1.14	14000	1.28
E	3.9	7100	6900	6900	1.12	11500	1.59
F	5.0	2000	2200	2400	1.17	7400	1.11
G	5.9	1000	*d*	1000	1.24	4800	1.13
H	6.2	1800	1900	1600	1.19	8300	1.19
I	6.1	2500	*d*	2400	1.23	10600	1.23
J	6.0	3500	3400	3600	1.21	14000	1.52

[a] SEC, size exclusion chromatography; M_n, number-average molecular weight; PDI, polydispersity index; MALDI-TOF, matrix-assisted laser desorption/ionization time-of-flight. [b] Determined from ^{1}H NMR (see Figure 6). [c] Poly(styrene) was used as a standard, and a correction factor, measured for linear poly(tetrahydrofuran), of 0.44 was used. [d] Not experimentally determined.

romethane (HPLC grade) was stored on calcium hydride and used after distillation from CaH_2. Allyl alcohol (AA; Merck >98%) was purified by distillation and was stored on molecular sieves (3 Å). Trifluoromethanesulfonic anhydride (Tf_2O; Acros 98%) was purified by distillation right before use. 2,6-Di-*tert*-butylpyridine (DTBP; Maybridge Chemicals >97%), MeOH (HPLC-grade), pentane (technical), NaOH (Acros), 9-borabicyclo[3.3.1]nonane (0.5 M in THF, Aldrich), and H_2O_2 (35 wt %, Acros) were used as received.

Synthesis of Allyl Functionalized Star-Shaped PTHF. A typical procedure for the polymerization of THF and in situ star formation was as follows. In a flame-dried, two-necked 50 mL flask, 7 mL of CH_2Cl_2, 1 mL of DTBP (4.46 mmol), and 0.5 mL of Tf_2O (2.97 mmol) were placed at 0 °C under a nitrogen atmosphere. AA (0.2 mL, 2.97 mmol) was added to this solution dropwise under vigorous stirring, and the mixture was stirred for 1 h. The initiator solution was brought to 20 °C, after which 20 mL of THF was added to start the polymerization (initiator concentration 0.105 mol·L^{-1}). Samples (100 μL, quenched in a small amount of MeOH) were withdrawn from the polymerization system at definite time intervals for ^{1}H NMR and SEC analysis. After the prescribed reaction time (4 min; conversion 27%), the polymerization was terminated by adding 0.074 mL of TAEA (0.496 mmol, six arms in this example), immediately followed by adding 1.25 mL of TMP (7.44 mmol). The ratios of TAEA and TMP were adapted according to the expected number of arms. The reaction was stirred at 20 °C for 1/2 h, after which the salts were filtered off. The polymer was then precipitated in cold pentane (−20 °C), filtered off on a cold glass filter, washed with cold pentane, and finally dried in a vacuum. ^{1}H NMR (δ in ppm, $CDCl_3$): 5.79 (m, $CH_2{=}CH{-}CH_2{-}O{-}$), 5.16 and 5.07 (d, $CH_2{=}CH{-}CH_2{-}O{-}$), 3.86 (d, $CH_2{=}CH{-}CH_2{-}O{-}$), 3.32 (b, $-O-CH_2CH_2CH_2CH_2-$), 2.2−2.95 (b, CH_2 in α-position of N), 1.51 (b, $-O-CH_2CH_2CH_2CH_2-$). $M_n = 8300$ g·mol^{-1}; polydispersity index (PDI) = 1.19.

Synthesis of Hydroxyl Functionalized Star-Shaped PTHF. A typical procedure for the conversion of terminal allyl groups to hydroxy groups was as follows. In a dry, two-necked 100 mL flask, 1 g of polymer (entry G, Table 1, 1.0 mmol allyl groups) and 40 mL of dry THF were placed at 0 °C under a nitrogen atmosphere. Then, 10 equivalents (equiv) of 9-borabicyclo[3.3.1]nonane (9-BBN) (10.0 mmol) was slowly added to this solution and the mixture was stirred for 2 h at 0 °C. Next, 10 equiv of NaOH (5 M solution in H_2O, 10.0 mmol) and H_2O_2 (10.0 mmol) was added. The reaction mixture was stirred for 24 h at room temperature and was then refluxed for 2 h. The polymer was purified by first evaporating all solvent. After this, the polymer was dissolved in CH_2Cl_2 and extracted three times with H_2O. After drying over $MgSO_4$, the polymer was precipitated from the CH_2Cl_2 solution in pentane as described above. ^{1}H NMR (δ in ppm, $CDCl_3$): 3.54 (t, $HO-CH_2-CH_2-CH_2-O-$), 3.51 (t, $HO-CH_2-CH_2-CH_2-O-$), 3.40 (b, $-O-CH_2CH_2CH_2CH_2-$), 1.86 (t, $HO-CH_2-CH_2-CH_2-O-$), 1.60 (b, $-O-CH_2CH_2CH_2CH_2-$).

Synthesis of Linear PTHF. In a flame-dried, two-necked 250 mL flask, 100 mL of THF was added under a nitrogen atmosphere. The solution was brought to 20 °C, after which the polymerization was started by adding 0.415 mL of Tf_2O (2.47 mmol). The polymerization was carried out at 20 °C for the prescribed reaction time (35 min) and was stopped by adding 1 mL of MeOH (24.7 mmol). The excess of THF was evaporated until a viscous solution was obtained. The polymer was then precipitated in ice-cold water, filtered off on a cold glass filter, and finally dried in a vacuum. ^{1}H NMR (δ in ppm, $CDCl_3$): 3.40 (b, $-O-CH_2CH_2CH_2CH_2-$), 3.32 (b, CH_3-O end group), 1.60 (b, $-O-CH_2CH_2CH_2CH_2-$). $M_n = 8000$ g·mol^{-1}; PDI = 1.15.

Methods of Analysis. ^{1}H NMR spectra were recorded in $CDCl_3$ at room temperature on a Bruker AM500 spectrometer at 500 MHz or on a Bruker Avance 300 at 300 MHz.

SEC was performed on a Waters instrument, with a refractive-index (RI) detector (2410 Waters), equipped with Waters Styragel HR3, HR4, and HR5 serial columns (5 μm particle size) at 35 °C. Polystyrene standards were used for calibration, and $CHCl_3$ was used as an eluent at a flow rate of 1.5 mL/min. Molecular weight and polydispersity index were determined using the Breeze Millennium software.

MALDI-TOF mass spectra were recorded on a Applied Biosystems Voyager DE STR MALDI-TOF spectrometer equipped with 2 m linear and 3 m reflector flight tubes and a 337 nm nitrogen laser (3 ns pulse). All mass spectra were obtained with an accelerating potential of 20 kV in positive ion mode and in linear and/or reflector mode. Dithranol and *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (BMPM) (20 mg·mL^{-1} in THF) were used as a matrix, LiCl or NaI (1 mg·mL^{-1}) was used as a cationating agent, and polymer samples were dissolved in THF (2 mg·mL^{-1}). Poly(ethylene oxide) standards ($M_n = 2000$ or 5000 g·mol^{-1}) were used for calibration. All data were processed using the Data Explorer (Applied Biosystems) and the Polymerix (Sierra Analytics) software package.

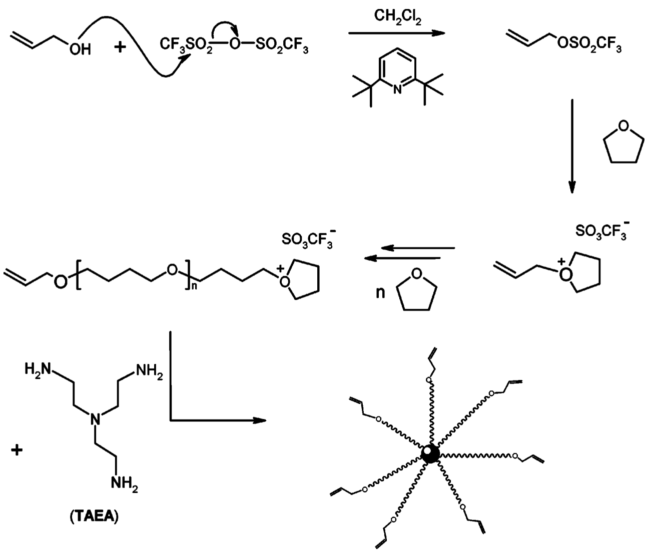
An Ubbelohde-type viscosimeter (capillary diameter 0.46 mm), thermostated at 25 °C, was used to measure solution viscosities, using THF as the solvent.

Results and Discussion

Synthesis and MALDI-TOF Study of Allyl Functionalized Star-Shaped PTHF. As depicted in Scheme 1, allyl terminated star-shaped PTHF was synthesized in two steps. First, the functional initiator, allyl triflate, was prepared in situ by reacting allyl alcohol with trifluoromethanesulfonic anhydride, in the presence of 2,6-di-*tert*-butylpyridine as a nonnucleophilic proton trap. The monomer was added to the reaction mixture, after which the polymerization started. Second, to obtain the star polymers, the living polymer chains were terminated with a multifunctional amine.[33] By changing the ratio of initiator to amine concentration, the number of arms of the star polymers could be varied between three and six (see below).

^{1}H NMR analysis of the initiating mixture, shown in Figure 1, proves that the allyl triflate is formed in high yield (>95%).

Scheme 1. Synthesis of Allyl Functionalized Star-Shaped Poly(tetrahydrofuran)



As described earlier, some diallyl ether formation can occur during this reaction.[28] Ether formation is due to reaction of the triflate ester with a second alcohol molecule. Since diallyl ether is inert during polymerization and the fraction of diallyl ether was below 5%, there was no noticeable influence on the polymerization.

Two different initiator concentrations (0.051 and 0.105 mol·L^{-1}) were examined to synthesize PTHF with different targeted molecular weights in high yield. Figure 2A shows that the first-order kinetic plots of the polymerizations are linear, indicating that the concentration of active species is constant for both concentrations. From the linear curve, the first-order rate constant can be calculated using the kinetic equation for the CROP of THF:[34,35]

$$\ln\frac{[M]_0 - [M]_e}{[M]_t - [M]_e} = k_p[I]_0 t$$

For an initiator concentration of 0.051 mol·L^{-1}, k_p was determined to be 0.0105 s^{-1}·mol^{-1}·L, while for 0.105 mol·L^{-1} k_p is 0.0112 s^{-1}·mol^{-1}·L. As both values are equal within experimental error, the reaction is about twice as fast for a doubled initiator concentration. This again demonstrates that, for both concentrations, initiation is efficient. Figure 2B shows the evolution of the number-average molar masses (M_n) (measured by SEC and NMR) as a function of conversion. M_n increases linearly with conversion, and the values are close to the theoretical values calculated assuming 100% initiation efficiency. However, PTHF with narrow PDI can only be obtained at low conversions because otherwise transfer reactions can occur, leading to dormant species.[36,37]

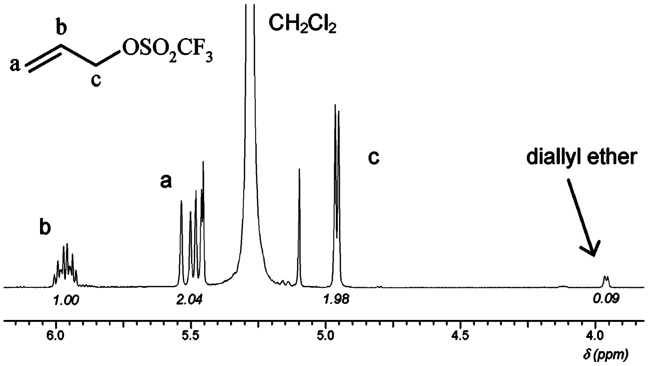


Figure 1. ^{1}H NMR (300 MHz) spectrum in $CDCl_3$ of the initiation mixture for the living cationic ring-opening polymerization of tetrahydrofuran using allyl alcohol and trifluoromethanesulfonic anhydride.

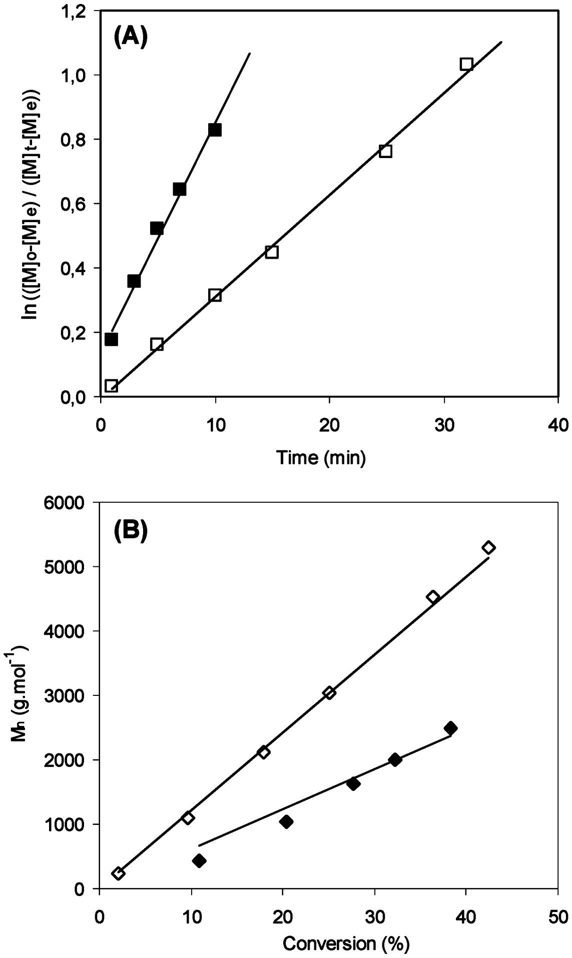


Figure 2. Kinetics of the polymerization of tetrahydrofuran using allyl alcohol (AA) as a functional initiator at 20 °C, $[M]_0 = 8.69$ mol·L^{-1}. (A) First-order plot: (□) [AA] = 0.051 mol·L^{-1}; (■) [AA] = 0.105 mol·L^{-1}. (B) Molecular weight (M_n) as a function of conversion: (◆, ◇) values measured by size exclusion chromatography for, respectively, [AA] = 0.105 and 0.051 mol·L^{-1}. Theoretical values are indicated with solid lines.

Before the polymerization was terminated with TAEA, a sample was taken and terminated with MeOH. In this way, the structure and the molecular weight of the arms from which the star polymer was built could be analyzed. The arms were analyzed with SEC, NMR, and MALDI-TOF. All three techniques confirmed that a living polymerization took place. Therefore, both molecular weight and functionality could be controlled. To illustrate this, the MALDI-TOF spectrum of a PTHF arm terminated with MeOH is depicted in Figure 3. Only one series of peaks, separated by 72 Da (mass of THF repeat unit) is detected. The similarity between the measured and the calculated isotope distribution confirms that this series can be attributed to the expected α-allyl-ω-methoxy functionalized PTHF. Also, the mass errors of the measured isotopes were below 10 ppm compared to the theoretically calculated values.

An overview of the results for the synthesis of reactive star-shaped PTHF is given in Table 1. Star-shaped structures with different numbers of arms (three to six) have been synthesized with narrow PDI and well-defined M_n. For example, Figure 4 shows the SEC traces of some star molecules (entries A and G) and the arms from which they have been built. The molecular

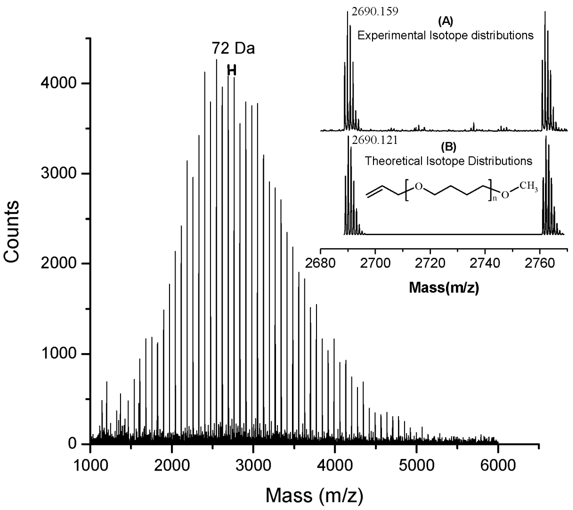


Figure 3. Matrix-assisted laser desorption/ionization time-of-flight mass spectrum in reflector mode of allyl functionalized poly(tetrahydrofuran). The experimental mass-resolved peaks for the Li-cationized series (A) is compared to the theoretical isotope distribution (B). Matrix, dithranol; cationating agent, NaI.

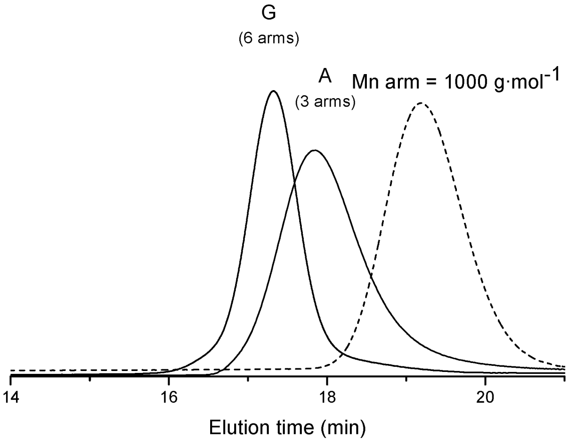


Figure 4. Size exclusion chromatography traces of entry products A and G (Table 1) and of the original poly(tetrahydrofuran) arm.

weight clearly increases for all stars. There are no shoulders at high elution volume (low M_n), which indicates that the reaction only consisted of living chains that have all been terminated by the multifunctional amine. Because of the smaller hydrodynamic volume of branched structures compared to linear analogues, the multiplication of the M_n of the arm by the number of arms is always higher than the M_n values of the star measured by SEC.[1]

If the molecular weight of the arms gets too high (entries E and J), efficient termination is no longer possible due to steric hindrance, which results in higher PDI values (>1.5). This can be observed in the SEC curves obtained from these star-shaped polymers (Figure 5). When termination is slow, the polymerization continues during a certain time interval and shoulders at low elution time (high M_n) are observed. To obtain well-defined star polymers, the maximum in molecular weight of a PTHF arm is limited by the number of arms. For four arms, for example, it is still possible to graft arms with a M_n of 6000 g·mol^{-1} (entry D), while for six arms inefficient termination occurs already with an M_n of 3500 g·mol^{-1} (entry J) (Figure 5).

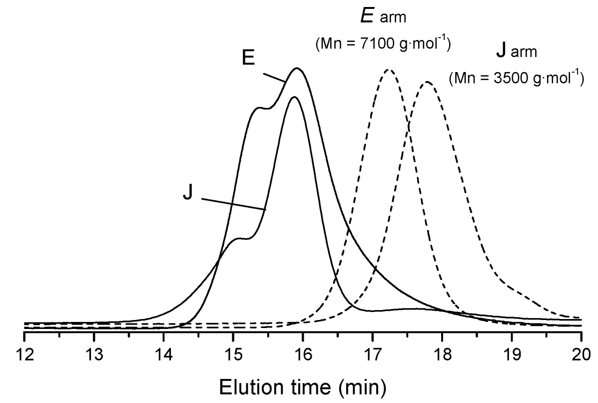


Figure 5. Size exclusion chromatography traces of entry products E and J (Table 1) and of the corresponding poly(tetrahydrofuran) arms.

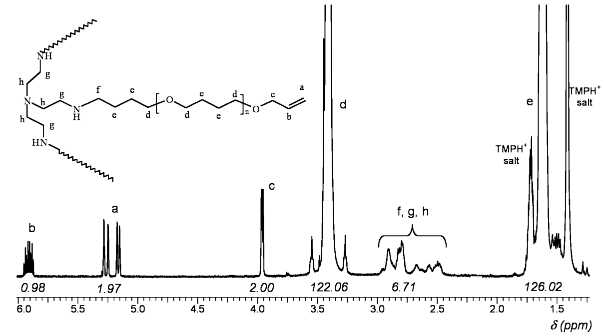


Figure 6. ^{1}H NMR spectrum (500 MHz) in $CDCl_3$ of entry C (Table 1, reactive star with three arms).

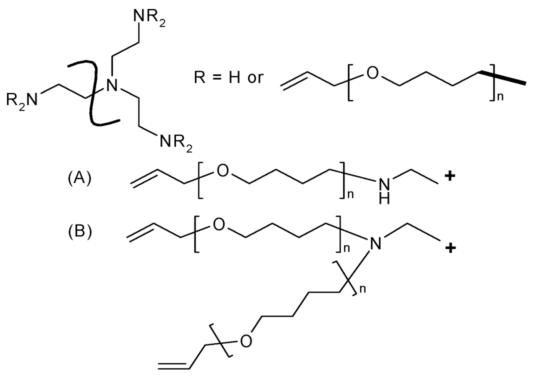
In Figure 6, the ^{1}H NMR of a star polymer with three arms (entry C) is given. The average number of arms is determined by comparing the integration of the protons in α-position of the nitrogens (f−h in Figure 6) to those of the allyl groups (a−c in Figure 6). The calculated values agree well with the values theoretically expected from the ratio of the reagents. This again proves that all of the living chains are completely terminated. From the ^{1}H NMR spectrum, it is also possible to determine M_n of the individual arms. By comparing the integration of the protons of the allyl groups (a−c in Figure 6, five H's) with the integration of the PTHF protons (d or e in Figure 6, four H's), the M_n of the arms could be calculated as follows:

$$M_n = \frac{\text{integration of PTHF protons}}{\text{integration of allyl protons}}(4/5)72 + 57 \tag{1}$$

in which 72 is the molar mass of a THF unit and 57 is the molar mass of the allyl end group. The values calculated in this way always agree well with the values obtained with SEC and MALDI-TOF analysis (Table 1).

The star-shaped structures were also analyzed by MALDI-TOF. These attempts initially failed for many sample preparation procedures (using dithranol as a matrix) because only signals at low molar mass (<3000 g·mol^{-1}) were obtained, which do not correspond to the star molecules. Since that distribution could also be measured without adding a cationizing agent (NaI), fragmentation of the amine-containing core of the star molecules was assumed. Scheme 2 proposes different fragmentation structures. Figure 7 compares the experimental and theoretical isotope distributions of the fragmentation region of a star polymer with six arms (entry G in Table 1) and of structure B in Scheme 2. The good correlation (mass error below 20 ppm) confirms that the amine-core of the star-shaped PTHF fragmentizes during the MALDI-process. For all of the star polymers, structure B in Scheme 2 could be detected. However, structure A was never found in the spectrum, not even for polymers with three arms.

Scheme 2. Possible Fragmentation of Star-Shaped Tris(2-aminoethyl)amine Core during Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Analysis



By changing the matrix to *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (BMPM), the laser intensity could be reduced.[38,39] This resulted in less fragmentation, which allowed us to visualize the distributions of the star molecules. This is illustrated in Figure 8 for a star with six arms (entry G from Table 1). Besides the fragmentation products between 1000 and 3000 g·mol^{-1}, a distribution appeared at the expected M_n of the star polymer (between 4500 and 8500 g·mol^{-1}). This is further confirmed by the good correlation between the theoretical and experimental isotope distributions of the allyl functionalized stars (inset, Figure 8). This is also reflected by the good agreement between the measured average mass (5889.21 Da) and the theoretical one (5889.71 Da; mass error 50 ppm). Surprisingly, no side series of stars with five or seven arms could be detected. Probably the formation of stars with seven arms is inhibited due to the creation of a positively charged species and due to steric hindrance. Hence, MALDI-TOF confirms the quantitative synthesis of allyl functionalized polymers with six arms. This is, to our knowledge, only one of the few examples in which MALDI-TOF mass spectroscopy could be used to confirm the existence of complex, polydisperse branched polymer structures.[40]

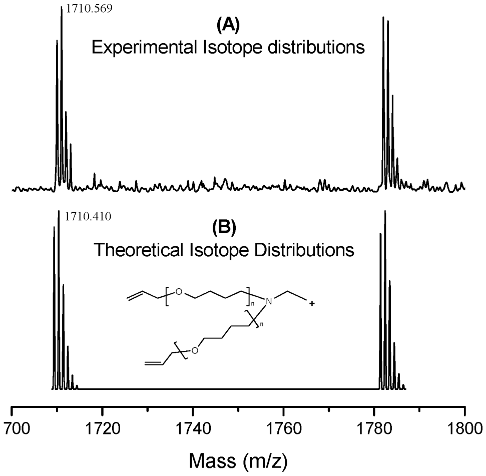


Figure 7. Comparison of experimental and theoretical isotope distributions of ion formed in the matrix-assisted laser desorption/ionization process due to fragmentation of the tris(2-aminoethyl)amine core. Matrix: *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile.

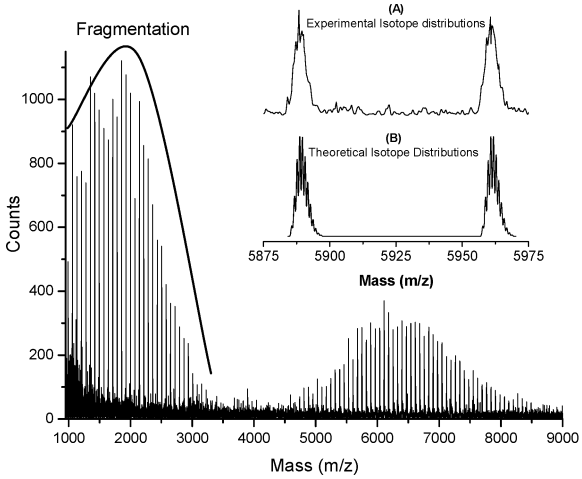
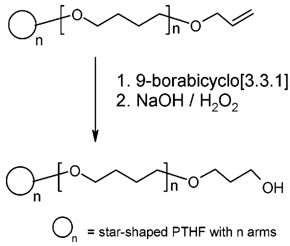


Figure 8. Matrix-assisted laser desorption/ionization time-of-flight mass spectrum of entry G (Table 1). In the inset, the experimental distribution for the Na-cationized star-shaped polymer with six arms is compared to the theoretical isotope distribution. Matrix, *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile; cationating agent, NaI.

Scheme 3. Transformation of Terminal Allyl Groups of Poly(tetrahydrofuran) Star Polymers into Hydroxy Groups



End Group Modification of Star-Shaped PTHF. The terminal allylic groups were transformed to hydroxy groups with 9-BBN in combination with a mixture of NaOH/H_2O_2, using the classical hydroboration/oxidation procedure (Scheme 3). The efficiency of the reaction was checked by ^{1}H NMR and MALDI-TOF. Figure 9 shows the ^{1}H NMR spectra of the starting product and the resulting hydroxy functionalized star-shaped PTHF. The characteristic signals at 3.80(t), 3.64(t), and 1.86(p) resulting from the CH_2 groups respectively in α-, γ-, and β-positions of the hydroxy group and the complete disappearance of the signals of the allylic protons demonstrate the quantitative formation of the expected hydroxy functionalized star-shaped PTHF. Also, MALDI-TOF results confirm the quantitative functionalization (Figure 10). Despite the fact that the star polymers fragmentize during the MALDI process, an isotopic resolution can be obtained for the fragmentation ions. By comparing the fragments of the allyl and the hydroxy functionalized star-shaped PTHFs,

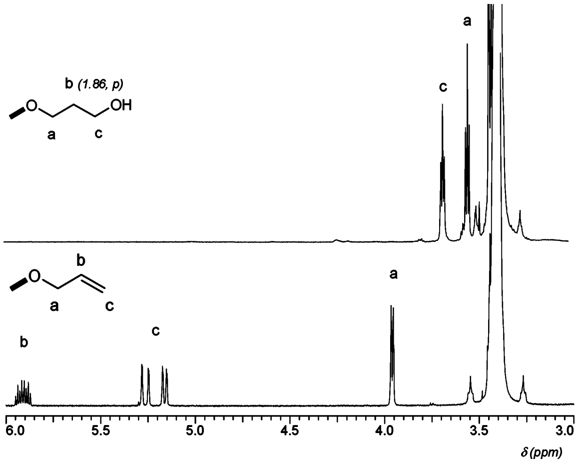


Figure 9. ^{1}H NMR spectra (500 MHz) in $CDCl_3$ of transformation of terminal allyl groups (bottom) of poly(tetrahydrofuran) star polymers into hydroxy groups (top).

Table 2. Intrinsic Viscosities and g' Values for Linear Poly(tetrahydrofuran) (PTHF) and Allyl Functionalized Star-Shaped PTHF[a]

sample	M_n(arm)	total M_n (g·mol^{-1})	$[\eta]_{exp}$[b] (mL/g)	$[\eta]_{linear}$[c] (mL/g)	$g' = [\eta]_{star}/[\eta]_{linear}$
linear		14000	42.1		
linear		8000	24.4		
linear		4100	12.5		
linear		2100	10.2		
star; 3 arms	1300	3900	12.7	15.7	0.81
star; 3 arms	2500	7500	21.3	25.2	0.84
star; 6 arms	1000	6000	13.4	21.4	0.63
star; 6 arms	2000	12000	22.8	35.5	0.64

[a] $[\eta]$, intrinsic viscosity; M_n, number-average molecular weight. [b] Measured in tetrahydrofuran at 25 °C. [c] $[\eta]_{linear} = (3.74 \times 10^{-2})M_n^{0.73}$.

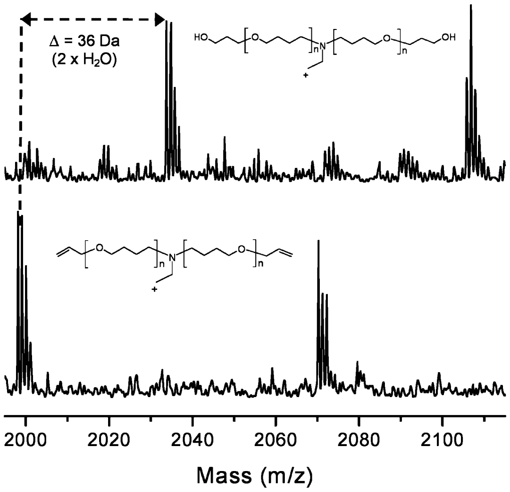


Figure 10. Matrix-assisted laser desorption/ionization time-of-flight results of transformation of terminal allyl groups (bottom) of poly(tetrahydrofuran) star polymers into hydroxy groups (top). Matrix, *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile; cationating agent, NaI.

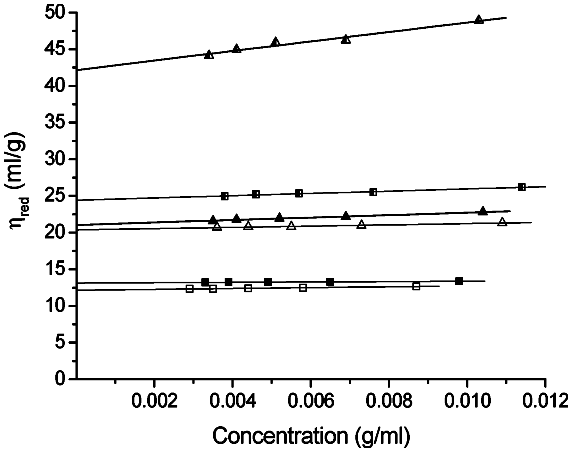


Figure 11. Reduced viscosity ($[\eta]$) as a function of concentration for different poly(tetrahydrofuran) (PTHF) samples in tetrahydrofuran at 25 °C. (◭) Linear PTHF, number-average molecular weight (M_n) = 14 000 g·mol^{-1}; (◧) linear PTHF, M_n = 8000 g·mol^{-1}. Allyl functionalized star-shaped PTHF: (▲) six arms, M_n(arm) = 2000 g·mol^{-1}; (△) three arms, M_n(arm) = 2500 g·mol^{-1}; (■) six arms, M_n(arm) = 1000 g·mol^{-1}; (□) three arms, M_n(arm) = 1300 g·mol^{-1}.

it can be seen that the distribution shifts exactly 36 Da, which corresponds to the mass of the addition of H_2O to each double bond.

Viscosity Properties of Allyl Functionalized Star-Shaped PTHF. Star-shaped polymers have different molecular dimensions compared to their linear analogues. This results, among other properties, in different solution properties, such as for example a lower intrinsic viscosity ($[\eta]$).[41] The dilute solution properties of the reactive PTHF stars compared to their linear analogues were investigated by measuring the reduced viscosity (η_{red}) as a function of concentration (Figure 11). The intrinsic viscosity can then be obtained by extrapolation of η_{red} to zero concentration. Clearly, the star molecules have a lower $[\eta]$ than their linear analogues. For example, $[\eta]$ of linear PTHF, M_n = 14 000 g·mol^{-1}, is about 2 times higher than the star with six arms, M_n = 12 000 g·mol^{-1}. The effect of branching on the molecular dimension in solution can also be expressed by using the experimental shrinkage factor g', defined as $[\eta]_{star}/[\eta]_{linear}$, where $[\eta]_{star}$ and $[\eta]_{linear}$ correspond respectively to the intrinsic viscosities of the star polymer and the linear polymer with the same M_n, measured under the same conditions.[41] $[\eta]_{linear}$ was calculated with the Mark–Houwink equation:

$$[\eta]_{linear} = (3.74 \times 10^{-2})M_n^{0.73} \qquad (2)$$

which was determined from the values obtained for the linear polymers (Table 2). The g' values for the stars with three and six arms are less than 1, which indicates that the stars have smaller molecular dimensions than linear polymers. As expected, the stars with six arms ($g' \cong 0.6$) are more compact than those with three arms ($g' \cong 0.8$). As predicted by theory and previous experiments, the g' values are independent of M_n and are only related to the number of arms.[41]

Conclusion

Reactive PTHF star polymers were successfully synthesized with CROP by a combination of functional initiation and the use of a multifunctional end capper. The stars were quantitatively functionalized with allyl end groups, and their structure was clearly identified by NMR and MALDI-TOF analysis. Branched structures containing three to six arms were obtained with a M_n up to 20 000 g·mol^{-1}. The terminal allyl groups were quantitatively converted into hydroxy groups, which for example could be used to prepare star block copolymers or for further derivatization. The reactive stars were further investigated by intrinsic viscosity measurements. The g' shrinkage factor derived from those measurements clearly confirmed the star-shaped structure.

The controlled synthesis and end group functionality of such reactive star-shaped polymers can induce interesting perspectives for the creation of nanoparticles and nanoporous layers, which is now under investigation.

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