Expanding the Supramolecular Polymer LEGO System: Nitroxide-Mediated Living Free-Radical Polymerization as a Tool for Mono- and Telechelic Polystyrenes

BAS G. G. LOHMEIJER, ULRICH S. SCHUBERT

Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology and Dutch Polymer Institute, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Received 22 February 2004; accepted 27 February 2004
DOI: 10.1002/pola.20189
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Nitroxide-mediated, controlled living radical polymerization was employed to introduce terpyridine ligands at one or two chain ends of polystyrene. For this purpose, a unimolecular initiator bearing both a terpyridine ligand as well as a mediating nitroxide was synthesized and used for the controlled polymerization of styrene. Moreover, a maleimide-functionalized terpyridine was prepared in order to synthesize telechelic polymers, utilizing nitroxide substitution reactions. Kinetic studies of the polymerization of styrene were carried out. In all polymerizations, special attention was focused on the retention of end-group functionality, in light of the effects of autoinitiation and autopolymerization. © 2004 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 42: 4016–4027, 2004

Keywords: nitroxide-mediated controlled radical polymerization (NMP); end-group functionality; maleimide; polystyrene; terpyridine; supramolecular; initiators; kinetics; nitroxide mediated controlled radical polymerization; polystyrene

INTRODUCTION

Supramolecular polymer chemistry has great potential for developing materials that combine the special features of both polymer and supramolecular chemistry:[1] the intrinsic material properties of a polymer backbone in combination with the self-organization, switching, and/or reversibility properties of supramolecular entities connected to that polymer backbone. The self-assembly process allows a large variety of "traditional" macromolecular architectures to be easily constructed.[2–8] Our current interests lie in linear block copolymer architectures, although we also have reported our investigations of graft copolymers and chain-extended homopolymers.[9,10] The construction of metallo-supramolecular AB diblock copolymers is based on inert metal complexes: a *bis*-terpyridine ruthenium complex serves as the supramolecular linker between two different blocks. The two-step self-organization process involves *mono*-complexation of one terpyridine end–functionalized polymer with $RuCl_3$ followed by *bis*-complexation of a second, differently substituted terpyridine ligand (Fig. 1).[11] Covalent block copolymers are well recognized for their striking morphologies:[12] the repulsive interactions between the blocks may give rise to a phase separation and a self-assembly process in which the constituting blocks form distinct phases. The resulting morphology depends on the volume fractions of the respective blocks and the strength of the repulsion between the two blocks. A low polydispersity in each block is a necessity to

Correspondence to: U. S. Schubert (E-mail: u.s.schubert@tue.nl)

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 42, 4016–4027 (2004)

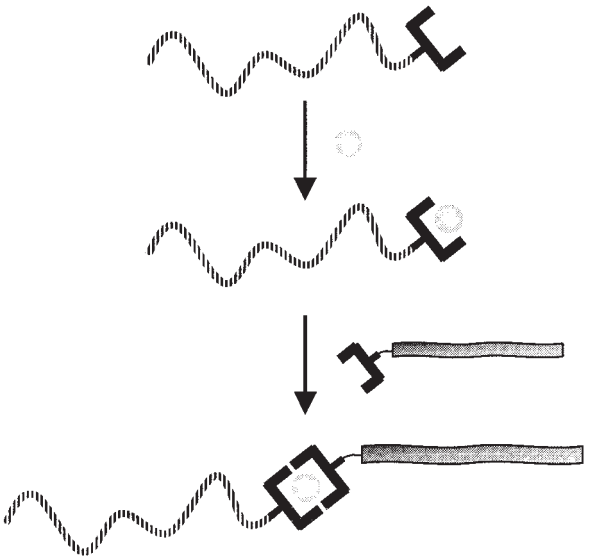
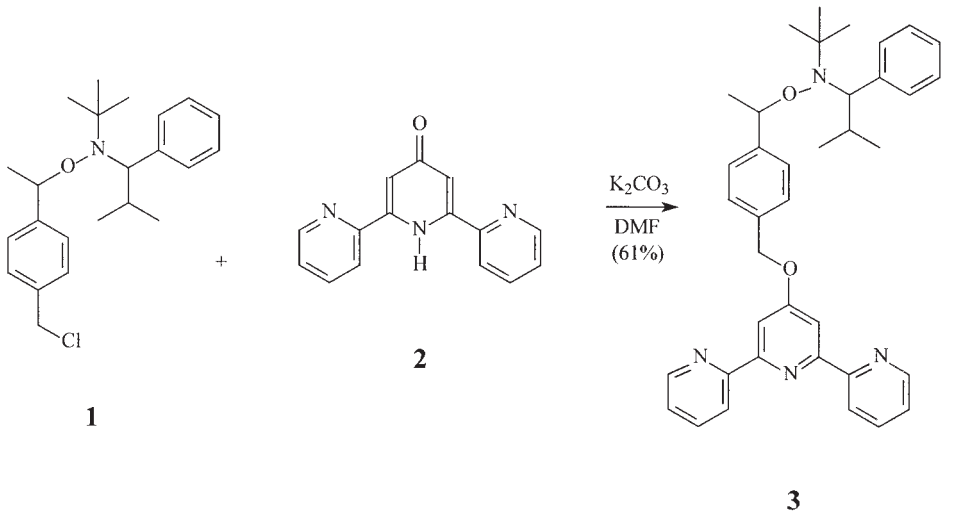


Figure 1. Schematic representation of the two-step synthesis of metallo-supramolecular block copolymers.

facilitate well-defined phase behavior.[13] For the preparation of metallo-supramolecular diblock copolymers an additional prerequisite is that the constituting blocks must contain a single terpyridine end group at one of the polymer chain ends.

Perfect control over the molecular architecture is therefore a must in the synthesis of such diblock copolymers. Thorough control over the molecular weight and its distribution can be gained by utilizing controlled living polymerization techniques. End-group functionalization of polymers prepared by anionic polymerization has been a valuable tool for us for the introduction of a terpyridine end group into polymers such as polystyrene, poly(ethylene oxide), poly(ethylene-*co*-butylene), and polystyrene-*b*-poly(2-vinylpyridine).[11,14,15] Nevertheless, the limited range of monomers, intolerance to functional groups (such as the terpyridine ligand), and stringent purification procedures call for polymerization techniques other than anionic ones. In the last decade important advances have been made in the field of controlled, living free-radical polymerization (CRP). Radical polymerization is widely employed in industry and academia because of its compatibility with functional groups and its tolerance to water. Moreover, since the development of such techniques as atom transfer radical polymerization (ATRP)[16] and reversible addition–fragmentation chain transfer (RAFT),[17] as well as nitroxide-mediated polymerization (NMP),[18] it has been possible to obtain polymers with narrow molecular weight distributions and high end-group functionality. CRP techniques can be used to polymerize complete monomer families, such as styrene, (meth)acrylates, acrylamides, acrylonitriles, dienes, and vinylpyridines. For our purposes, ATRP unfortunately is not suitable: the terpyridine ligand would compete for the transition metal ion of the ATRP catalyst and control would be lost. Of course, the terpyridine ligand could be protected by forming an inert complex, and after polymerization decomplexation would give terpyridine-functionalized polymers, but such a pathway is rather tedious and unnecessary. RAFT is the most versatile controlled radical polymerization technique, but thorough end-group control is still a major challenge.[19] In NMP, however, control over the end groups can be gained relatively easily by using a functional unimolecular initiator.[20] Some termination in the beginning of a polymerization process initiated by such an initiator leads to an excess of persistent nitroxide radicals. This excess mediates in an equilibrium reaction between propagating (growing) and dormant chains: the dormant chains are reversibly turned into growing chains by continuous addition and fragmentation of the nitroxide radical, allowing an equal growth rate of each polymer chain until high conversions.[21] Hawker developed a universal alkoxyamine with a chloro functionality capable of polymerizing styrene, acrylates, dienes, acrylamides, and vinylpyridines.[20,22,23] After some synthetic perseverance we were able to reproduce this compound. In a subsequent step 2,6-*bis*-($2_{3'}$-pyridyl)-4-pyridon[24,25] was reacted with this alkoxyamine yielding a unimolecular initiator bearing the terpyridine moiety (Scheme 1). In this way we acquired an initiator that already contains the terpyridine ligand: polymerizations initiated by this unimolecular initiator therefore will lead automatically to polymers containing one terpyridine ligand at the chain end, at least in theory. In descriptions of nitroxide-substitution reactions in the literature, the use of maleimides was reported as particularly promising.[26,27] So we prepared a maleimide-functionalized terpyridine that we envisioned would give rise to terpyridine telechelic polymers and, with the subsequent addition of metal ions, to chain-extended supramolecular polymers, ABA- and AB_n metallo-supramolecular block copolymers. In this contribution we present the detailed results of our study on the polymerization of styrene, which aimed at making polymers of different mo-



1 2 3

Scheme 1. Schematic representation of the preparation of the terpyridine-functionalized initiator suitable for nitroxide-mediated controlled living free-radical polymerization. Compounds **1** and **2** were synthesized according to procedures in the literature.

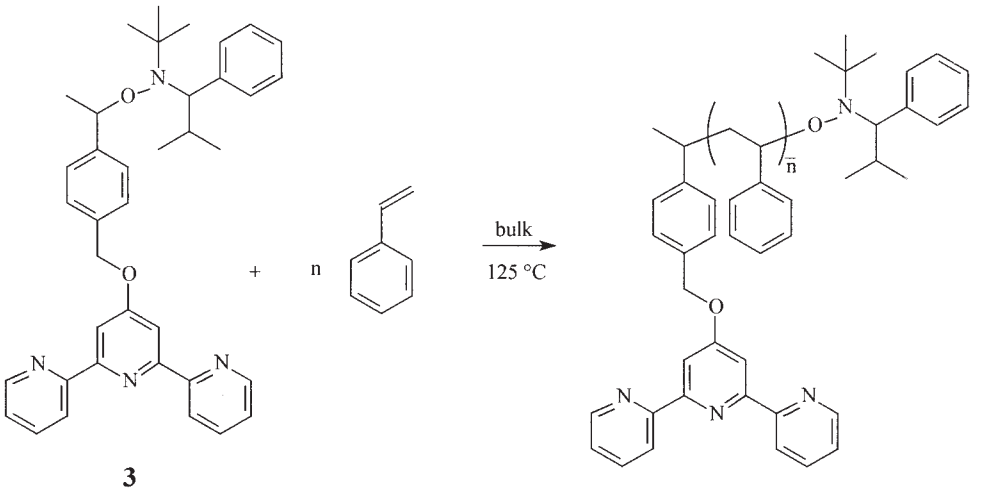
lecular weights, with a special focus on the end-group functionality of the polystyrenes.

EXPERIMENTAL

Chemicals were received from Aldrich, Acros, and Fluka and were used without further purification unless stated otherwise. Solvents were bought from Biosolve. Column chromatography was carried out on flash silica and/or deactivated neutral AlOx. ^{1}H NMR were recorded on a Varian Inova spectrometer with a frequency of 500 MHz at 25 °C, ^{1}H NMR and ^{13}C NMR on a Varian Mercury spectrometer with frequencies of 400 and 100 MHz respectively at 25 °C, and on a Varian Gemini spectrometer with frequencies of 300 and 75 MHz at 25 °C, respectively. Chemical shifts are given in ppm downfield from tetramethylsilane. UV–vis spectra were recorded on a Perkin Elmer Lambda 45P spectrophotometer. Matrix-assisted laser desorption/ionization time-of-flight mass spectra (MALDI–TOF MS) were obtained using dithranol as the matrix and NaI on a PerSeptive Biosystems Voyager DE PRO spectrometer using a layer-by-layer spotting technique. Size exclusion chromatography was conducted on a 30-cm-long PL mixed-D column. Analysis was carried out with an RI detector (Shimadzu RID-10A) and a UV–vis detector (SPD-10Avp) at 275 nm. Chloroform, which was the eluent, had 4% Et_3N and 2% isopropanol as additives to reduce column interaction of the free terpyridine ligand[28] at a flow of 1.0 mL/min using a Shimadzu LC-10Avp pump. Polystyrene standards were used for calibration. IR spectra were measured on a Perkin Elmer 1600 Fourier transform infrared spectrometer in attenuated total reflection (ATR) mode. Elemental analysis was carried out on a Perkin Elmer 2400 Series CHN analyzer.

Synthesis of Terpyridine Functional Initiator (3), 2,2,5-Trimethyl-3-{1-[4′-(4″-terpyridinyloxy)methyl]phenylethoxy}-4-phenyl-3-azahexane

To a suspension of 2,6-*bis*-(2′-pyridyl)-4-pyridon **2** (7.50 g, 0.030 mol) and K_2CO_3 (14.70 g, 0.110 mol) in 75 mL of dry dimethylformamide (DMF) at 50 °C, a solution of 2,2,5-trimethyl-3-(1-(4′-chloromethyl)phenylethoxy)-4-phenyl-3-azahexane[20] **1** (10.65 g, 0.029 mol) in dry DMF (25 mL) was added dropwise. Stirring was continued overnight, after which the reaction mixture was cooled, poured into cold water (500 mL) and extracted with CH_2Cl_2 (3 × 300 mL). The combined organic layers were dried over Na_2SO_4, filtered, and removed *in vacuo*. The light brown residue was subjected to a filtration column (AlOx, hexane:CH_2Cl_2, 1:1) and recrystallized twice from ethanol, yielding 10.15 g (61%) of a polycrystalline white powder. The presence of diastereomers loosened the normally well-defined *J* couplings in the terpyridine region, fine-splitting into ddd or



3

Scheme 2. Synthesis of terpyridine-functionalized polystyrene utilizing terpyridine functional initiator **3**.

dt, with only multiplets or doublets remaining. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, both diastereomers): 8.69 (m, 4H, $H_{6,6''}$), 8.62 (d, 4H, J = 7.5 Hz, $H_{3,3''}$), 8.17 (s, 2H, $H_{3',5'}$, major), 8.16 (s, 2H, $H_{3',5'}$, minor), 7.82 (t, 4H, J = 7.0 Hz, $H_{4,4''}$), 7.57–7.18 (m, 22H, aromatic and $H_{5,5''}$) 5.35 (s, 2H, tpyOCH_2, minor), 5.30 (s, 2H, tpyOCH_2, major), 4.97 (q + q, 2H, J = 6.0 Hz, HC—O—N, both diastereomers), 3.47 (d, 1H, J = 10.5 Hz, O—N—CH, major), 3.36 (d, 1H, J = 10.5 Hz, O—N—CH, minor), 2.38 (m, 1H, CH_3CHCH_3, major) 1.67 (d, 3H, J = 6.0 Hz, CH_3CH—O—N, major), 1.58 (d, 3H, J = 6.0 Hz, CH_3CH—O—N, minor), 1.43 (m, 1H, CH_3CHCH_3, minor), 1.34 (d, 3H, J = 6.0 Hz, CH_3CHCH_3, major), 1.08 [s, 9H, C(CH_3)$_3$, minor], 0.93 (d, 3H, J = 6.0 Hz, CH_3CHCH_3, major), 0.81 [s, 9H, C(CH_3)$_3$, major], 0.56 (d, 3H, J = 6.0 Hz, CH_3CHCH_3, minor), 0.21 (d, 3H, J = 6.0 Hz, CH_3CHCH_3, minor). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): 166.9 ($C_{4'}$), 157.0 ($C_{2',6'}$), 155.9 ($C_{2,2''}$), 148.9 ($C_{6,6''}$), 145.7, 144.9, 142.3, 142.1 (q, C aromatic), 136.7 ($C_{3',5'}$), 135.0, 134.3 (q, C aromatic), 130.9, 130.8, 127.3–126.1 (C—H aromatic), 123.7 ($C_{3,3''}$), 121.3 ($C_{4,4''}$), 107.7, 107.6 ($C_{5,5''}$), 83.1 (C—O—N, major), 82.3 (C—O—N, minor), 72.1 (O—N—C, major), 72.0 (O—N—C, minor), 69.9 (tpyOCH$_2$, major), 69.8 (tpyOCH$_2$, minor), 60.4 [C(CH$_3$)$_3$, major], 60.3 [C(CH$_3$)$_3$, minor], 31.9, 31.6, 28.3 [C(CH$_3$)$_3$, minor], 28.2 [C(CH$_3$)$_3$, major], 24.5, 23.0, 22.0, 21.9, 21.1, 20.9. UV–vis (CH_2Cl_2): λ/nm (ϵ/L mol^{-1} cm^{-1}): 278 (20,100), 240 (25,300). IR (ATR) ν (cm^{-1}): 3060 (CH_2, CH_3); 2973, 2868 (CH); 1600, 1582, 1563 (C—C, C—N terpyridine), 1516, 1468, 1385, 1354, 1195, 1063, 1015, 821, 793, 743, 733, 701. MALDI–TOF MS (dithranol) *m/z*: 587 (M + H$^+$, 80%), 336 (M$^+$ nitroxide, 20%). ELEM. ANAL. Calcd for $C_{38}H_{42}N_4O_2$ (586.400 g/mol): 77.83% C, 7.22% H, 9.55% N; found, 77.94% C, 7.18% H, 9.34% N.

Synthesis of *N*-(4′-Terpyridinyl)pent-5-oxy)maleimide (5)

(a) A solution of 1-amino-5-(4′-terpyridinyl)oxypentane[29] **4** (5.16 g, 15 mmol) and maleic anhydride (1.47 g, 15 mmol) in dry *p*-xylene (50 mL) was refluxed overnight, while the produced water was removed by a Dean–Stark trap. After the reaction, the solvent was removed *in vacuo*. The brown residue was subjected to column chromatography (AlOx, CH_2Cl_2), and the product was isolated as a white solid (1.73 g, 28%). (b) Mitsunobe coupling: a solution of Ph_3P (0.393 g, 1.50 mmol) in dry THF (20 mL) was cooled to −78 °C. DIAD (0.313 g, 1.55 mmol) was added over 2–3 min. To the yellow reaction mixture 1-hydroxy-5-(4′-terpyridinyl)oxypentane (0.544 g, 1.62 mmol) was added, followed by neopentylalcohol (0.073 g) and subsequently by maleimide (0.146 g, 1.50 mmol). The resulting suspension was stirred for 5 min, after which the reaction mixture was allowed to heat up to room temperature and stirred overnight. THF was removed *in vacuo,* and the residue was purified by column chromatography (AlOx, hexane:EtOAc 1:2, gradually increasing to EtOAc), yielding an off-white solid (116 mg, 19%). TLC analysis showed one spot; however, judging

from the ^{1}H NMR and elemental analyses, the compound was not pure. No further purification efforts were undertaken because route (a) was less time-consuming and more straightforward. ^{1}H NMR ($CDCl_3$): 8.68 (dt, 2 H, J = 4.8, 1.5 Hz, $H_{6,6''}$), 8.60 (dt, 2 H, J = 7.2, 1.6 Hz, $H_{3,3''}$), 7.99 (s, 2 H, $H_{3',5'}$), 7.83 (ddd, 2 H, J = 7.2, 4.8, 1.6 Hz, $H_{4,4''}$), 7.31 (ddd, 2 H, J = 7.2, 4.8, 1.6 Hz, $H_{5,5''}$), 6.68 (d, 2H, J = 0.4 Hz, H vinylic), 4.21 (t, 2H, J = 8.0 Hz, OCH_2) 3.56 (t, 2H, J = 9.2 Hz, NCH_2), 1.89 (m, 2H, OCH_2CH_2), 1.68 (m, 2H, NCH_2CH_2), 1.52 (m, 2H, $CH_2CH_2CH_2$). ^{13}C NMR ($CDCl_3$): 170.7 (*C*O), 167.1 ($C_{4'}$), 156.9 ($C_{2',6'}$), 156.0 ($C_{2,2''}$), 148.9 ($C_{6,6''}$), 136.6 ($C_{3',5'}$), 133.9 (*C* vinylic), 123.7 ($C_{3,3''}$), 121.2 ($C_{4,4''}$), 107.2 ($C_{5,5''}$), 67.7 (OCH_2), 37.5 (NCH_2), 28.4 (OCH_2CH_2), 28.1 (NCH_2CH_2), 23.2 ($CH_2CH_2CH_2$). UV–vis (CH_2Cl_2): λ/nm (ϵ/L mol^{-1} cm^{-1}): 279 (24,400), 243 (24,900). IR (ATR) ν (cm^{-1}): 3083, 3069, 3014 (aliphatic), 2938, 2908, 2865 (vinylic, aromatic), 1698 (C═O), 1601, 1581, 1562 (tpy C—C, C—N), 1467, 1452, 1441, 1407, 1370, 1350, 1331, 1203, 1156, 1113, 1092, 1086, 1045, 1032, 989, 841, 791, 743, 729, 705, 690. MALDI–TOF MS (dithranol) *m/z*: 415 (M + H$^+$, 100%). ELEM. ANAL. Calcd for $C_{24}H_{22}N_4O_3$: 69.55% C, 5.35% H, 13.52% N; found, 69.14% C, 5.43% H, 13.48% N.

General Procedure for Polymerization of Styrene

Styrene was subjected to an AlOx filtration column before use in order to remove the inhibitor. A stock solution of the initiator in 25 mL of purified styrene (0.210 mol) was prepared. For a degree of polymerization (DP) of 125, 250, and 500, the corresponding amounts of initiator were 0.968 g (166 mmol), 0.499 g (85 mmol), and 0.247 g (42 mmol), respectively. For a DP of 800, 0.128 g (21 mmol) was dissolved in 20 mL of purified styrene. For the various kinetic investigations, the stock solution was transferred to 7–9 reaction vessels. Three freeze-pump-thaw cycles were applied for removal of oxygen before the reaction vessels were immersed in an oil bath of 125 °C. The polymerization was carried out for a certain amount of time and then stopped. In total eight polymerization times were used for polymerization of the same stock solution. The conversion was measured gravimetrically. Molecular weights and polydispersity indices were measured by size exclusion chromatography, whereas ^{1}H NMR was used for the determination of end-group functionality and molecular weight by careful integration of the polymer backbone to the terpyridine signals. Purification by column chromatography of terpyridine-functionalized from nonfunctionalized polystyrene was carried out on silica, eluting first with hexane:CH_2Cl_2 (1:3), then CH_2Cl_2 and finally increasing the gradient with THF. For an M_n above 10,000 g/mol of the terpyridine-functional polystyrene, adding THF was unnecessary. Analytical data are for polystyrene with M_n = 7700 g/mol and PDI = 1.08. ^{1}H NMR ($CDCl_3$): 8.68 (m, broad, 2H, $H_{6:6''}$), 8.62 (m, broad, 2H, $H_{3:3''}$), 8.21 (m, broad, 2H, $H_{3':5'}$), 7.93 (m, broad, 2H, $H_{4:4''}$), 7.47–6.32 (m, broad, 353H, $H_{PS\ backbone\ aromatic}$; $H_{aromatic\ nitroxide}$, $H_{5,5''}$), 5.34 (m, broad, 2H, tpyOCH_2), 4.27–4.07 (broad, 1H, *H*C—O—N), 3.50–3.15 (broad, 1H, O—N—C*H*), 2.45–0.53 [m, broad, 225H, $H_{PS\ backbone\ aliphatic}$; $C(CH_3)_3$; CH_3CHCH_3; $CH_{3\ initiating\ fragment}$]. GPC (UV) M_n (PDI): 7700 g/mol (1.08).

Procedure for Preparation of α,ω-Maleimido Terpyridine-Functionalized Polystyrene

Terpyridine-functionalized polystyrene (after purification by column chromatography, 300 mg, 4 mmol) and **5** (66 mg, 16 mmol) were heated under argon at 100 °C in degassed *t*-butylbenzene for 2 h. The temperature was then increased to 125 °C, and heating was continued for another 4 h. The solution was allowed to cool to room temperature and precipitated into methanol. The white precipitate was isolated and reprecipitated from THF into methanol. Yield: 240 mg (78%). ^{1}H NMR ($CDCl_3$): 8.67 (m, broad, 4H, $H_{6:6''}$), 8.61 (m, broad, 4H, $H_{3:3''}$), 8.18 (m, broad, 2H, $H_{3':5',\ initiating\ fragment}$), 7.98 (s, broad, 2H, $H_{3':5',\ maleimide}$), 7.37–6.21 (m, broad, 349H, $H_{PS\ backbone\ aromatic}$; $CH_{maleimide}$, $H_{5,5''}$), 5.28 (m, broad, 2H, tpyOC$H_{2,\ initiating\ fragment}$), 4.19 (m, broad, tpyOC$H_{2,\ maleimide}$), 3.70 (m, broad, 2H, NC$H_{2,\ maleimide}$), 2.28–0.60 (m, broad, 215H, $H_{PS\ backbone\ aliphatic}$; $CH_{2,\ maleimide}$; $CH_{3,\ initiating\ fragment}$). GPC (UV) M_n (PDI): 7800 g/mol (1.09). MALDI–TOF MS (dithranol) M_n (PDI): 7180 g/mol (1.04).

RESULTS AND DISCUSSION

Terpyridine-Functionalized Initiator

Scheme 1 shows the synthesis of terpyridine-functionalized initiator **3**. Chloromethyl derivate **1** and pyridon **2** were synthesized as described previously.[20,26,27] K_2CO_3, a mild base, deprotonated **2** and then underwent an S_N2 reaction with **2**. Given the easy workup procedures, that is, only

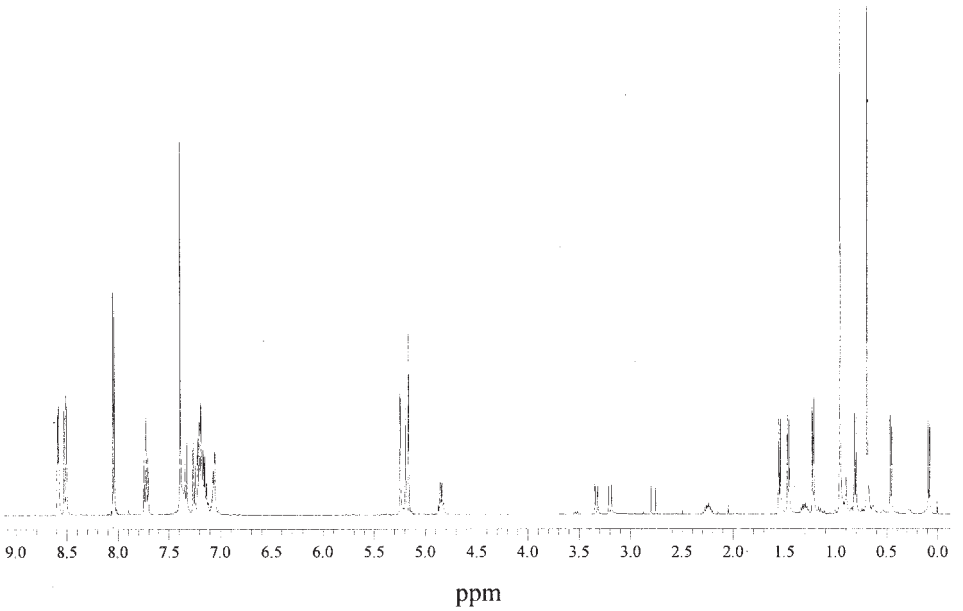


Figure 2. ^{1}H NMR of the terpyridine-functionalized initiator in $CDCl_3$. Typical terpyridine signals are visible between 8.8 and 7.2 ppm. From the ^{1}H NMR, the molar ratio of the diastereoisomers was calculated as 45:55.

a filtration column, pyridon **2** was used in excess: it sticks to AlOx using CH_2Cl_2 as a solvent, whereas the product is easily washed down. The first fraction obtained contained a small amount of some impurity that was present in **1** and was discarded. The second and largest fraction contained the desired compound, unimolecular initiator **3**. Figure 2 shows the ^{1}H NMR, where the typical terpyridine signals are visible between 8.8 and 7.2 ppm. Also, the signal of the CH_2 connecting the terpyridine to the styrene fragment has shifted from 4.66 to 5.35 ppm with relation to the chloromethyl derivative. Because the initiator contains two stereo-centers, four isomers can be expected. The diastereoisomers show different signals in ^{1}H NMR and are present in a 45:55 ratio. Further assignment was carried out using 2D NMR techniques. Although conformational changes are obvious, no large influence has been reported in initiating efficiency of the stereoisomers, making their separation unnecessary.[30]

Polymerization of Styrene

Scheme 2 shows the synthesis of polystyrene using the terpyridine functionalized initiator. A stock solution of the initiator in purified styrene was prepared and transferred to eight reaction vessels for kinetic investigations. Three freeze-pump-thaw cycles were applied for the removal of oxygen before the reaction vessels were immersed in an oil bath of 125 °C. The polymerization was carried out for a certain amount of time and then stopped. In total eight polymerization times were used for the polymerization of the same stock solution. All analysis of the kinetics (conversion, molecular weight) was carried out before the samples were precipitated (twice). Again, the respective molecular weights were determined (GPC, ^{1}H NMR), and several precipitated samples were subjected to column chromatography. Table 1 displays some of the results. Figure 3 shows an example of a ^{1}H NMR spectrum of terpyridine-functionalized polystyrene. The integration of the terpyridine signals into the polymer backbone was used to determine M_n. A few general remarks can be made about the data shown in Table 1: (1) high conversions could be reached; (2) the theoretical molecular weights are in good agreement with the observed ones, and (3) polydispersities are well below 1.3.

The molecular weights as measured by ^{1}H NMR for polystyrene were systematically higher than those measured by GPC. The latter technique used polystyrene standards for calibration and therefore should have been more accurate if column interactions were ruled out. Of course, the higher the I_n, the less accurate ^{1}H NMR will be.

Table 1. A Selection of Results Obtained by Polymerization of Styrene by the Terpyridine-Functionalized Initiator

M_n, th (g/mol)	Polymerization Time (min)	Conversion (%)	M_n (GPC)	PDI (GPC)	M_n (^{1}H NMR)
7000	75	54	4700	1.12	5600
10,000	200	77	7300	1.08	7700
12,500	240	77	8900	1.11	10,300
25,000	600	86	19,700	1.12	22,400
50,000	360	66	34,500	1.13	41,200
80,000	360	69	55,600	1.33	87,400

M_n, th represents the targeted molecular weight (100% conversion). M_n data in the table are before any purification procedures.

Nevertheless, all spectra were recorded with a long relaxation time (10 s), and sufficient scans were applied (128) until no differences were found upon integration. An explanation for the nonfitting data from GPC and ^{1}H NMR may be found in the autoinitiation of styrene. The early literature on nitroxide-mediated polymerization (using TEMPO) includes some reports on this topic.[31–34] However, recently this issue seems to have been neglected because polymerization times have been shortened drastically, thus seeming to reducing the effect of autoinitiation. But this does not mean there will be no autoinitiation and subsequent autopolymerization. Autoinitiation and autopolymerization using a terpyridine-functionalized initiator lead to two types of polymers: one with a terpyridine end group and the other with no functionality. Both polymers should show controlled growth: the nitroxide radical has no preference for the propagating radical and the corresponding initiator fragment. To account for these two types of polymers, polystyrene of M_n = 7300

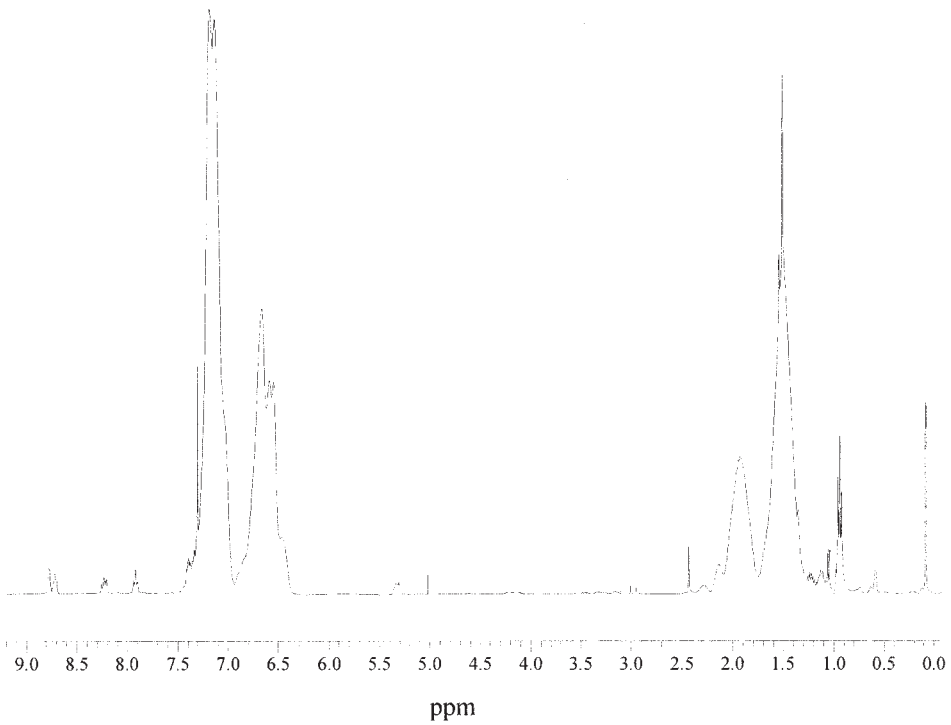


Figure 3. ^{1}H NMR spectrum in $CDCl_3$ of terpyridine-functionalized polystyrene of M_n = 7700 g/mol and PDI = 1.08.

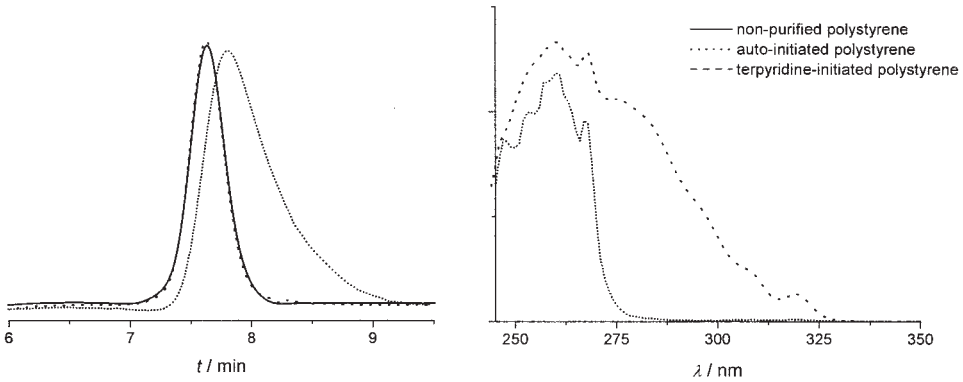
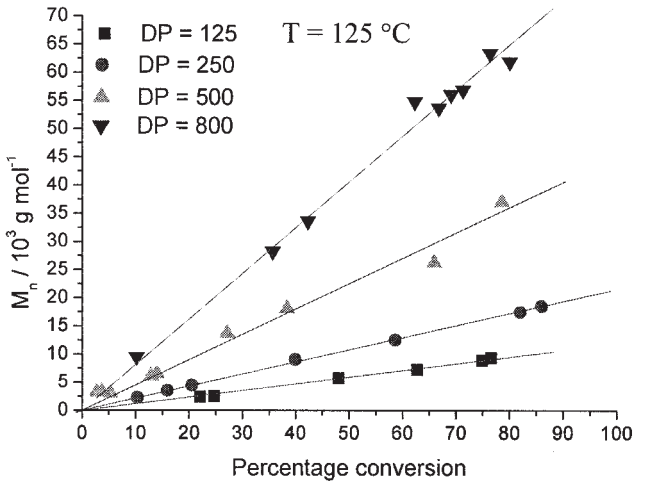
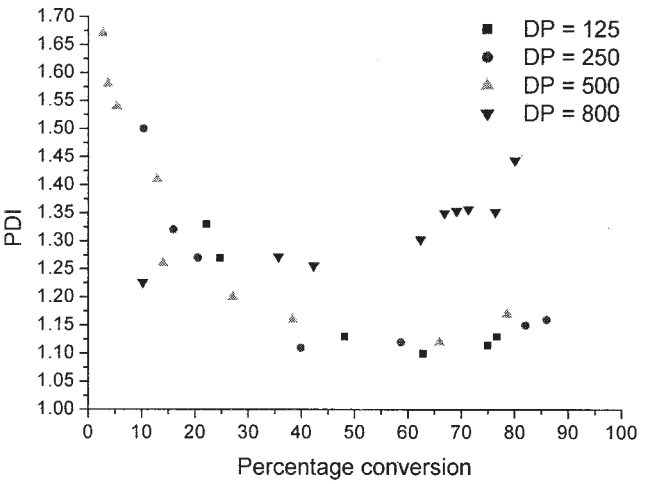


Figure 4. GPC traces of polystyrene before and after separation by column chromatography in two fractions (3 traces, left) and the corresponding UV spectra as measured by a photodiode array detector (PDA) of the two fractions (right). The GPC trace of the nonseparated polystyrene is added to show that autoinitiated chains are not detected by UV–vis because of the low amount present and the much lower optical density as compared to terpyridine-initiated polystyrene.

g/mol and PDI = 1.08 (entry 2 in Table 1) was subjected to column chromatography (for conditions, see the Experimental section). The first fraction, which was the minor component (<5% by weight), contained the nonfunctionalized polystyrene, whereas the second fraction contained the terpyridine-functionalized polymer. The starting material and the two obtained fractions were subjected to GPC analysis using a photodiode array detector. Figure 4 shows the GPC chromatograms and the accompanying UV spectra from the photodiode array detector. The UV spectra clearly demonstrate the presence of two end groups, as the terpyridine ligand has a characteristic absorption from 260 to 300 nm. Moreover, the M_n's and PDIs of the two polymer fractions were calculated: the terpyridine-containing polymer had an M_n of 7700 g/mol, as expected, and a PDI of 1.08, indicating living and controlled growth of the terpyridine-initiated chains. On the other hand, the nonfunctional polystyrene had an M_n of 3200 g/mol and a PDI of 1.42. To study the effects of autoinitiation upon targeted molecular weight, a more detailed look at the kinetics of the polymerization of styrene was undertaken. Four degrees of polymerization (DPs) were targeted (125, 250, 500, and 800), and for each a stock solution of the purified monomer containing the respective calculated amount of initiator was prepared. This stock solution was transferred to different reactors and polymerized at 125 °C for different times. The results are shown in Figures 5 and 6. A linear increase in molecular weight with conversion and a linear increase in conversion with time were observed. This indicates that all polymers were growing at the same rate and shows the controlled nature of the polymerization of styrene until at least 80,000 g/mol. It also shows that autoinitiation does not influence the pseudolivingness of the polymerization. Interestingly, the polymerization rates showed some striking differences: for DP = 250, 500, and 800, the rates were comparable, but for DP = 125 the polymerization rate was quite different. How can this be explained? For the first three DPs the rate was in good agreement with the thermal self-polymerization of styrene.[34] Rate of polymerization is independent of the initiator concentration because the concentration of persistent and propagating radicals remains more or less constant. Important to note is that the effects of autoinitiation become more important at higher DPs. There are fewer growing chains and fewer persistent radicals with an increasing $[M]/[I]$ ratio. Termination reactions thus become more important at lower radical concentrations. Because autoinitiation of styrene is a relatively slow process,[35,36] polymerization remains controlled: the increase in the number of growing radicals is automatically counteracted by termination reactions. In this fashion, the less that regulating nitroxide is present, the higher is the influence of autoinitiation and its concomitant termination reactions. The experimental results reflect this as shown by looking at the chains initiated by the terpyridine fragment: the molecular weights as measured by GPC and NMR were quite different. This obviously stems from the molecular weight by NMR



(a)



(b)

Figure 5. Plots of (a) molecular weight and (b) polydispersity index as a function of conversion for four targeted degrees of polymerization: DP = 125, 250, 500, and 800.

being calculated from the integration of the terpyridine initiator signal to the backbone, whereas by GPC this was not end-group related and thus better represented the actual molecular weight. On increasing the targeted molecular weight, the discrepancy between the measured molecular weights became larger, indicating that more autoinitiated chains were participating in the polymerization. Moreover, this discrepancy increased with increasing conversion. Also, the GPC chromatograms of the kinetic investigation for DP = 800 clearly showed tailing because of the more pronounced termination reactions. As a result, the polydispersity indices for this particular kinetic investigation remained rather high compared to the other kinetic runs. As stated before, the polymerization rate of DP = 125 was quite different than the other polymerization rates. This indicates non-steady-state polymerization, where the persistent radical effect is still operative. For such a case, Fischer described a $t^{2/3}$ dependence of $\ln([M_0]/[M])$: a continuous decrease of the propagating radicals through termination gives rise to this dependency.[37] Indeed, fitting the data with the $t^{2/3}$ time dependence revealed a perfect linear relationship. Interestingly, at the point when the propagating radicals reach a concentration similar to that of under thermal self-polymerization conditions, it would be expected that autoinitiation would start to play a role again. However, before this point was reached, monomer conversion apparently had proceeded too far for DP = 125.

On increasing the targeted molecular weight, a crossover from controlled to uncontrolled growth of the polymer chains was apparent, at which point the price to pay was the control over polydispersity and initiating group functionality. A simple way of decreasing the influence of autoinitiation would be to lower the temperature. Unfortunately, polymerization times increase tremendously because the propagation rate is reduced as is the rate for the homolytic C—O bond cleavage.

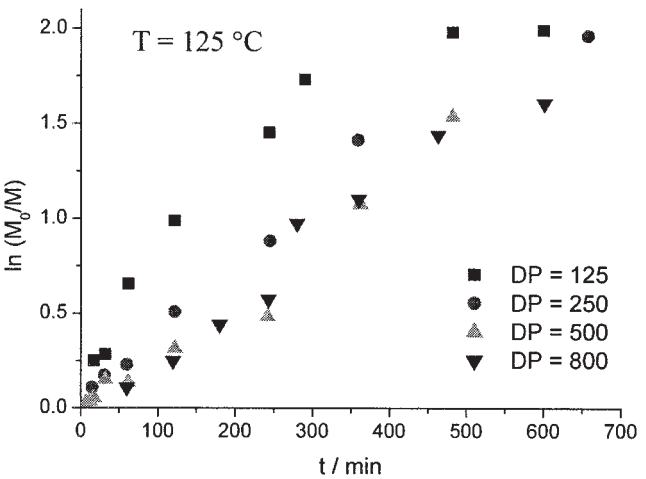
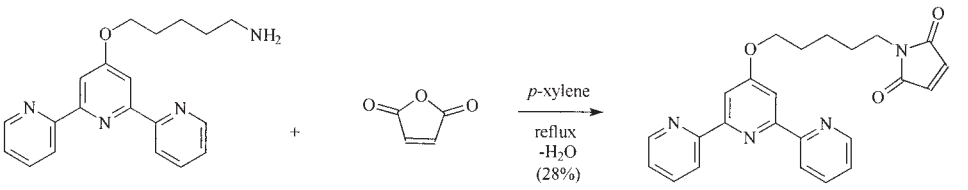


Figure 6. Plot of $\ln([M_0/M])$ as a function of time for four targeted degrees of polymerization: DP = 125, 250, 500, and 800.



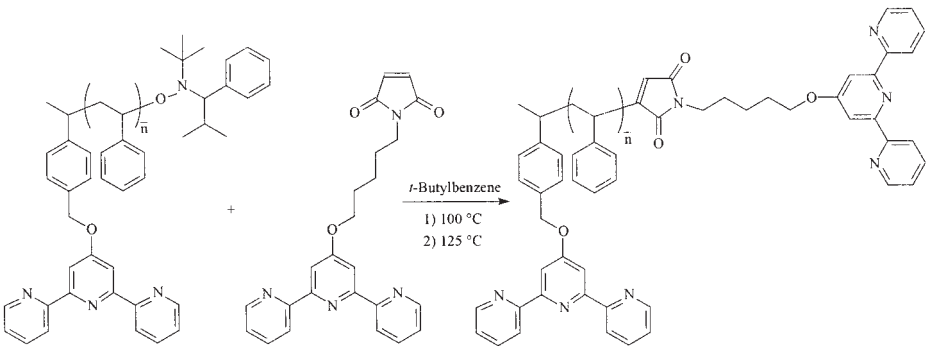
4 5

Scheme 3. Synthesis of terpyridine-modified maleimide **5**.

The question remains whether autoinitiation is really no longer an issue. For our purposes, the molecular weight range and corresponding polydispersities are already acceptable enough to serve as building blocks for metallo-supramolecular block copolymers.

Nitroxide Substitution for Telechelic Polystyrene

The nitroxide end group was still fully present for the lower-molecular-weight species, as can be judged from ^{1}H NMR, even after column chromatography. This again opens possibilities for further end-functionalized polystyrene prepared in this way. Covalent diblock copolymers can and have been prepared by other groups using the dormant nitroxide radical at the chain end as macroinitiator.[18,20,22,23,38,39] In this study we focused on end-group functionalization: if the dormant chain is again thermally initiated, the terminal styrene radical can be reacted with a maleimide.[26,27] Maleimides resist homopolymerization, therefore allowing facile functionalization of nitroxide end capped polymers because only one maleimide will be added to the chain. Enough maleimide in excess of the nitroxide is a must for preventing chain coupling. Moreover, the intermediate in which the maleimide group is capped by the nitroxide must give rise to a clean and high-yielding disproportionation reaction. In the literature it has been reported that this reaction has been exploited to introduce fluorescent labels at the chain end and/or to improve thermal stability.[26,27] Other radical addition reactions were reported by Matyjaszewski.[40] To prepare telechelic polystyrene bearing a terpyridine ligand at each chain end, a terpyridine-functionalized maleimide is required as building block. This compound was prepared by refluxing the corresponding amine-functionalized terpyridine **4** with maleic anhydride in *p*-xylene (Scheme 3).[41] Although the yields were not that good, the purification procedure was straightforward using an AlOx filtration column. Mitsunobe coupling[42] utilizing hydroxy-functional terpyridine and maleimide was tried as well, but the yields were not better after purification. We used the purified polystyrene (M_n = 7700 g/mol) for further modification by the terpyridine-functionalized maleimide **5** in order to obtain telechelic polystyrene (Scheme 4). In the literature this maleimide modification reaction was described in two steps: first the polymer and the maleimide are heated at 100 °C for 2 h in order to prepare the intermediate, and then



5

Scheme 4. Synthesis of *bis*-terpyridine-functionalized polystyrene.

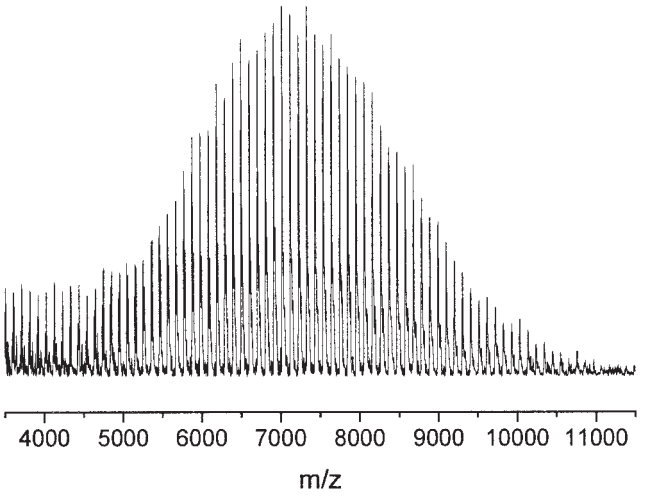


Figure 7. MALDI–TOF mass spectrum of α,ω-terpyridine telechelic polystyrene after nitroxide substitution by a terpyridine-functionalized maleimide.

the temperature is increased to 125 °C to establish the disproportionation. The reaction was carried out in DMF. However, in our hands the product contained only 60% *bis*-functionalized polymers as judged from ^{1}H NMR, which may have occurred because of chain transfer to the solvent. We therefore changed the solvent to *t*-butylbenzene, which is known for its low transfer constant, while all other conditions remained unchanged. With this solvent, the terpyridine-functionalized maleimide was incorporated much better, >95% as judged from the ^{1}H NMR. The GPC chromatogram showed no higher-molecular-weight shoulders, which would be indicative of chain coupling. Accordingly, the molecular weight and polydispersity did not change significantly (7800 g/mol, PDI = 1.09). Using MALDI–TOF MS we were able to identify the end groups of the *bis*-functionalized polystyrene as well as a shift of 194 mass units from the starting nitroxide polymer (Fig. 7), although the starting nitroxide-functionalized polystyrene showed depolymerization during the MALDI process as a function of the laser intensity. Trying to suppress depolymerization effects using various matrices previously has been subject of investigation.[43,44] Currently, the stability of alkoxyamines under MALDI conditions is under investigation using polystyrenes and initiators of lower M_n.

CONCLUSIONS

In conclusion, nitroxide-mediated controlled living free-radical polymerization (NMP) has proven to be an efficient tool for the preparation of polymers with one terpyridine end group when using a terpyridine-functionalized initiator. The initiator gave rise to polymers with relatively low polydispersities and high end-group functionalities for the monomers involved. However, it must be stressed that autoinitiation, which has been investigated in detail for styrene, limits the usefulness of the technique: the higher the targeted molecular weight and the more autoinitiated chains, the lower the end-group functionality and the worse polydispersity. Separation of the terpyridine functionalized from the nonfunctionalized polystyrene proved possible up to a molecular weight of ~20,000 g/mol. Telechelic terpyridine-functionalized polystyrene was prepared by a nitroxide substitution reaction utilizing a terpyridine-functionalized maleimide. These compounds will prove to be of great value for the preparation of AB and ABA metallo-supramolecular block copolymers. Moreover, this initiator is capable of controlling the polymerization of a variety of other vinylic monomers, opening a large field of building blocks. Also, terpyridine-functionalized block copolymers can be prepared by using the resulting polymers as macroinitiators. Synthetic pathways to metallo-supramolecular ABC and ABCD block copolymers are currently being developed.

The authors thank Dr. A. W. Bosman for very helpful discussions, M. A. R. Meier for MALDI–TOF MS and GPC analyses, H. Eding for elemental analysis, and the Dutch Council for Scientific Research (NWO) and the Fonds der Chemischen Industrie for funding.

REFERENCES AND NOTES

1. Lehn, J.-M. Makromol Chem Macromol Symp 1993, 69, 1–17.
2. Lohmeijer, B. G. G.; Schubert, U. S. J Polym Sci Part A: Polym Chem 2003, 41, 1413–1427.
3. Brunsveld, L.; Folmer, B. J. B.; Sijbesma, R. P.; Meijer, E. W. Chem Rev 2001, 101, 4071–4097.
4. Lamba, J. J. S.; Fraser, C. L. J Am Chem Soc 1997, 119, 1801–1802.
5. Smith, A. P.; Fraser, C. L. Macromolecules 2002, 35, 594–596.
6. Kelch, S.; Rehahn, M. Macromolecules 1999, 32, 5818–5828.
7. Kelch, S.; Rehahn, M. Chem Commun 1999, 1123–1124.
8. Schütte, M.; Kurth, D. G.; Linford, M. R.; Colfen, H.; Möhwald, H. Angew Chem Int Ed 1998, 37, 2891–2893.

9. Calzia, K. J.; Tew, G. N. Macromolecules 2002, 35, 6090-6093.
10. Schubert, U. S.; Hofmeier, H. Macromol Rapid Commun 2002, 23, 411–415.
11. Lohmeijer, B. G. G.; Schubert, U. S. Angew Chem Int Ed 2002, 41, 3825–3829.
12. Hamley, I. W. In The Physics of Block Copolymers; Oxford University Press: Oxford, UK, 1998.
13. Hadjikristidis, N. In Block Copolymers, Synthetic Strategies, Physical Properties and Applications; Wiley Interscience: Hoboken, NJ, 2003.
14. Schubert, U. S.; Hien, O.; Eschbaumer, C. Macromol Rapid Commun 2000, 21, 1156–1161.
15. Gohy, J.-F.; Lohmeijer, B. G. G.; Varshney, S. K.; Decamps, B.; Leroy, E.; Boileau, S.; Schubert, U. S. Macromolecules 2002, 35, 9748–9755.
16. Xia, J.; Matyjaszewski, K. Chem Rev 2001, 101, 2921–2990.
17. Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. Macromolecules 1998, 31, 5559–5562.
18. Hawker, C. J.; Bosman, A. W.; Harth, E. Chem Rev 2001, 101, 3661–3688.
19. D'Agosto, F.; Hughes, R.; Charreyre, M.-T.; Pichot, C.; Gilbert, R. G. Macromolecules 2003, 36, 621–629.
20. Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. J Am Chem Soc 1999, 121, 3904–3920.
21. Fischer, H. Chem Rev 2001, 101, 3581–3610.
22. Benoit, D.; Harth, E.; Fox, P.; Waymouth, R. M.; Hawker, C. J. Macromolecules 2000, 33, 363–370
23. Bosman, A. W.; Vestberg, R.; Heumann, A.; Fréchet, J. M. J.; Hawker, C. J. J Am Chem Soc 2003, 125, 715–728.
24. Constable, E. C.; Ward, M. D. J Chem Soc Dalton Trans 1990, 1405–1406.
25. Schubert, U. S.; Schmatloch, S.; Precup, A. A. Design Monom Polym 2002, 5, 211–221.
26. Rodlert, M.; Harth, E.; Rees, I.; Hawker C. J. J Pol Sci Part A: Polym Chem 2000, 38, 4749–4763.
27. Harth, E.; Hawker, C. J.; Fan, W.; Waymouth, R. M. Macromolecules 2001, 34, 3856–3862.
28. Lohmeijer, B. G. G.; Schubert, U. S. Macromol Chem Phys 2003, 204, 1071–1078.
29. Newkome, G. R.; He, E. J Mater Chem 1997, 7, 1237–1244.
30. Marque, S.; Le Mercier, C.; Tordo, P.; Fischer, H. Macromolecules 2000, 33, 4403–4410.
31. Malmstrom, E.; Miller, R. D.; Hawker, C. J. Tetrahedron 1997, 53, 15225–15236.
32. Matyjasewski, K.; Gaynor, S.; Greszta, D.; Mardare, D.; Shigemoto, T. Macromol Symp 1995, 98, 73–89.
33. Georges, M. K.; Kee. R. A.; Veregin, R. P. N.; Hamer, G. K.; Kazmaier, P. M. J Phys Org Chem 1995, 8, 301–305.
34. Fukuda, T.; Terauchi, T.; Goto, A.; Ohno, K.; Tsuji, Y.; Miyamoto, T.; Kobatake, S.; Yamada, B. Macromolecules 1996, 29, 6393–6398.
35. Souaille, M.; Fischer, H. Macromolecules 2002, 35, 248–261.
36. Greszta, D., Matyjaszewski, K. Macromolecules 1996, 29, 7661–7670.
37. Fischer, H. J Polym Sci Part A: Polym Chem 1999, 37, 1885–1901.
38. Hawker, C. J. J Am Chem Soc 1994, 116, 11185–11186
39. Fukuda, T.; Terauchi, T.; Goto, A.; Ysujii, Y.; Miyamoto, T.; Shimizu, T. Macromolecules 1996, 29, 3050–3052.
40. Coessens, V.; Pyun, J.; Miller, P. J.; Gaynor, S. G., Matyjaszewki, K. Macromol Rapid Commun 2000, 21, 103–109.
41. Coleman Jr., L. E.; Bork. J. F.; Dunn Jr., H. J Org Chem 1959, 24, 135–136.
42. Walker, M. A. J Org Chem 1995, 60, 5352–5355.
43. Dourges, M.-A.; Charleux, B.; Vairon, J.-P.; Blais, J.-C.; Bolbach, G.; Tabet, J.-C. Macromolecules 1999, 32, 2495–2502.
44. Burguiere, C.; Dourges, M.-A.; Charleux, B.; Vairon, J.-P. Macromolecules 1999, 32, 3883–3890.