Synthesis of aromatic carboxyl functionalized polymers by atom transfer radical polymerization†

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Abstract: The synthesis of aromatic carboxyl functionalized polymers by atom transfer radical polymerization is described. The α-bromo-p-toluic acid (1) initiated polymerization of styrene in the presence of copper(I) bromide and 2,2’-bipyridyl affords quantitative yields of the corresponding aromatic carboxyl functionalized polystyrene (2). Polymerization proceeded via a controlled free radical process to afford quantitative yields of the corresponding aromatic carboxyl functionalized polymers with predictable molecular weights ($M_n = 1600–25\,900\,g\,mol^{-1}$), narrow molecular weight distribution ($M_w / M_n = 1.1–1.40$) and an initiator efficiency above 0.87. The polymerization process was monitored by gas chromatographic analysis. The functionalized polymers were characterized by thin layer chromatography, size exclusion chromatography, spectroscopy, potentiometry and elemental analysis.

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INTRODUCTION

The uses and formulations of low molecular weight functionalized polymers with well defined molecular weight and polymer architecture, especially telechelic polymers, are widely investigated in industry and academia in several areas such as chain extension reactions, reversible ionic association, reactive processing, catalysis, drug delivery and compatibilization of polymer blends.$^{1,2}$

Atom transfer radical polymerization (ATRP) provides an efficient method for the synthesis of styrene, methyl methacrylate and acrylonitrile polymers with controlled molecular weight, molecular weight distribution, chain functionality, polymer architecture and composition.$^{3}$ The classical ATRP method encompasses the reversible homolytic cleavage of a carbon–halogen bond of an alkyl halide initiator molecule, such as 1-phenylethyl chloride, catalysed by a transition metal salt such as cuprous chloride, complexation with suitable ligands such as 2,2’-bipyridyl, followed by successive monomer insertion into the carbon halogen bond.$^{4,5}$ The structure of the polymer obtained by ATRP contains a halogen atom at the α-terminal end group with the initiator fragment at the α-terminus. Thus, the versatility of the ATRP technique facilitates the synthesis of telechelic polymers by the utilization of functionalized initiators for the controlled, living polymerization of styrene and methyl methacrylate. A plethora of functionalized initiators were employed in the initiation of styrene polymerizations by ATRP methods to afford polystyrene functionalized with end groups such as hydroxyl, epoxy, aryl bromide and primary amino groups.$^{6–11}$

In the classical ATRP process, neither the polymerization of carboxylic acid containing monomers nor the synthesis of carboxyl functionalized polymers are considered synthetically viable, because poisoning of the transition metal–ligand catalyst complex system is observed due to the rapid reversible formation of copper(I) carboxylates.$^{11–16}$ In addition, the presence of copper(I) carboxylates and carboxylic acids influences the rate of polymerization of the metal catalysed controlled radical polymerization of styrene.$^{11–16}$ Haddleton et al.$^{12}$ reported that the 2-bromoisobutyrate initiated polymerization of methyl methacrylate, catalysed by the (N-α-butyl-2-pyrrolidinemethanimine) copper(I) bromide system, proceeded with good control of molecular weight and molecular weight distribution. However, upon the addition of stoichiometric amounts of benzoic acid relative to initiator, the rate of polymerization was enhanced with concomitant broadening of the molecular weight distribution, indicating the poisoning of the copper–ligand catalyst system and low initiation efficiency. Also, reports by Perceo and co-workers$^{13}$ show that the addition of

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sodium benzoate to the CuCl/bpy catalysed living radical polymerization initiated by p-methoxybenzene sulfonyl chloride enhances the rate of polymerization of butyl acrylate in diphenyl ether. However, poor control of molecular weight is observed, and polymers with broad molecular weight distribution are formed. In addition, Zhang and Matyjaszewski\textsuperscript{16} reported that, in the ATRP of styrene by 1-phenylethyl bromide in the presence of benzoic acid, dark blue solutions were observed in the polymerization process, consistent with literature data that carboxylic acids coordinate strongly with copper(II) species and only weakly with copper(I) species.\textsuperscript{17} Furthermore, at low concentrations of benzoic acid (0.5 equivalents of benzoic acid to initiator), no significant effect on the polymerization of styrene was observed, and well defined polymers with low polydispersity were obtained. However, at higher concentrations of benzoic acid, decrease in the polymerization rate and broadening of the molecular weight distribution were observed. Thus, literature results indicate that the carboxylic acid group plays an active role in the metal-catalysed living radical polymerization of styrene and acrylate monomers, especially at high concentrations. The initial role of the carboxylic acid is to complex with the copper(I) centre, displacing the ligand, thereby creating a coordination site on the cuprate intermediate for propagation to occur.\textsuperscript{12-16}

Nevertheless, well defined polystyrene with terminal carboxylic acid groups can be prepared via ATRP methods using initiators with carboxylic acid groups remote to the initiator halogen end. Zhang and Matyjaszewski\textsuperscript{16} reported the synthesis of carboxyl functionalized polystyrene with low polydispersity and initiator efficiency of 0.7 using 4-(1-bromoethyl)benzoic acid as an initiator, were added and the heterogeneous mixture was degassed three times by freeze-pump-thaw cycles. Under an argon atmosphere, the reaction mixture was heated to 130 °C with a hold time of 3 min, followed by an increase in temperature to 280 °C at a rate of 10 °C min\textsuperscript{-1}. THF was used as internal standard.

For the determination of the molecular weights and molecular weight distributions of polymers, size exclusion chromatographic analysis was performed at a flow rate of 1 ml min\textsuperscript{-1} in THF at 30 °C using a Waters Alliance SEC autosampler equipped with a Phenogel guard column and a Phenogel column (5 µ, 500 Å pore size, 1K-15K MW range, 300 mm × 7.8 mm) in series with refractive index and dual angle laser light scattering detectors, after calibration with standard polystyrene samples (Aldrich Chemical Co), where applicable. \textsuperscript{1}H NMR (CDCl\textsubscript{3}) and \textsuperscript{13}C NMR (CDCl\textsubscript{3}) spectra were recorded on a Varian Gemini 200 spectrometer. Thin layer chromatographic analysis was performed on silica gel plate (Mercck, silica gel 60 F 254). Infrared spectra were recorded on a Perkin Elmer 883 infrared spectrophotometer. Concentrations of carboxylic acid chain-ends were determined by potentiometric titration of 0.1 g polymer sample in toluene with standardized methanolic sodium hydroxide using phenolphthalein as indicator.\textsuperscript{20} Elemental analysis was performed at the University of Cape Town.

### Polymerization

**Method**

The atom transfer radical polymerization of styrene polymerization in solution was carried out in Schlenk flasks under dry argon. In a typical procedure, copper(I) bromide (0.3260 g, 0.0023 mol), 2,2'-bipyridyl (1.06 g, 0.0068 mol) and dry diphenyl ether (5 ml) were added to a Schlenk flask. The reaction mixture was stirred for 5 min. Freshly distilled styrene (8 ml), followed by x-bromo-p-toluidic acid (0.4951 g, 0.0023 mol) as an initiator, were added and the heterogenous mixture was degassed three times by freeze-pump-thaw cycles. Under an argon atmosphere, the reaction mixture was heated to 130 °C for 12 h, with stirring. Upon cooling and addition of tetrahydrofuran (10 ml), the green solution was purified by passage through a short silica gel column to remove copper and ligand impurities. The polymer solution was concentrated in vacuo and precipitated into methanol to obtain white powder and drying over molecular sieves before use. Tetrahydrofuran (THF) (Aldrich Chemical Co) was purified as described previously.\textsuperscript{18,19} x-Bromo-p-toluidic acid (Aldrich Chemical Co) and CuBr (Aldrich Chemical Co) were used as received. 2,2'-Bipyridyl (Aldrich Chemical Co) was purified by recrystallization from n-hexane.\textsuperscript{3} Diphenyl ether (Aldrich Chemical Co) was used as received.

### EXPERIMENTAL

**Materials**

Styrene (Aldrich Chemical Co) was purified by drying over calcium hydride followed by vacuum distillation and drying over molecular sieves before use. Tetrahydrofuran (THF) (Aldrich Chemical Co) was purified as described previously.\textsuperscript{18,19} x-Bromo-p-toluidic acid (Aldrich Chemical Co) and CuBr (Aldrich Chemical Co) were used as received. 2,2'-Bipyridyl (Aldrich Chemical Co) was purified by recrystallization from n-hexane.\textsuperscript{3} Diphenyl ether (Aldrich Chemical Co) was used as received.
afford the functionalized polymer in the carboxylate form. The aromatic carboxyl functionalized polymer (2) was isolated by precipitation several times from THF solution into methanol containing 1% aqueous hydrochloric acid, filtered off and vacuum dried. Elemental analysis, \( \text{HOOCC}(\text{C}_6\text{H}_4)\text{CH}_2[\text{CH}_2\text{CH} (\text{C}_6\text{H}_4)\text{Br}: \text{Calc}, \text{C} 88.86\%, \text{H} 7.47\%; \text{found}, \text{C} 89.31\%, \text{H} 7.79\%.

**Kinetics**

The kinetics of styrene polymerizations were measured in the bulk and in solution with diphenyl ether as solvent. In a typical procedure, copper(I) bromide (0.0626 g, 0.0004 mol), 2,2'-bipyridyl (0.1363 g, 0.0009 mol) and dry diphenyl ether (10 ml) were added to a Schlenk flask. The reaction mixture was stirred for 5 min. Freshly distilled styrene (10 ml, 0.0873 mol) followed by \( \alpha \)-bromo-\( \beta \)-toluic acid (0.4951 g, 0.0023 mol) were added and the heterogenous mixture degassed three times by freeze-pump-thaw cycles. An aliquot (1 ml) of the sample, withdrawn from the reaction mixture using a stainless steel syringe, was dissolved in THF (9 ml) and subjected to gas chromatographic analysis to determine the amount of styrene in the sample at time, \( t = 0 \). Under argon atmosphere, the mixture was heated to 130 °C. At different time intervals, 1 ml aliquots were withdrawn from the flask under argon atmosphere and diluted with a known volume of THF (9 ml). The residual styrene content was determined by gas chromatographic analysis. Upon completion of the analysis, the polymer samples were purified by passage through a short silica gel column to remove catalyst impurities followed by precipitation from THF solution into methanol. The functionalized polymers were reprecipitated several times from THF solution into methanol, filtered off and vacuum dried.

**RESULTS AND DISCUSSION**

**Polymerization reaction**

Scheme 1 illustrates the general synthetic pathway for the \( \alpha \)-bromo-\( \beta \)-toluic acid initiated polymerization of styrene in diphenyl ether as solvent. In a typical procedure, copper(I) bromide catalyst and 2,2'-bipyridyl ligand. The polymerization proceeded via a controlled free radical process to afford quantitative yields of the corresponding aromatic carboxyl functionalized polystyrenes with predictable molecular weights (1) and narrow molecular weight distribution (2). To illustrate the synthetic utility of aromatic carboxyl functionalized initiators in ATRP, \( \alpha \)-bromo-\( \beta \)-toluic acid (1) was employed as functionalized initiator in the polymerization of styrene in solution in the presence of copper(I) bromide and 2,2'-bipyridyl at a molar ratio of [CuBr]0:[1]0:[Bpy]0 = 1:0.18 mol l\(^{-1}\). No dark blue colouration of the reaction mixture was observed upon the addition of the initiator (1), suggesting that no coordination of the carboxylic acid groups and the transition metal catalyst occurred during polymerization. However, as evidenced by FTIR analysis, the functionalized polymer was initially isolated as the copper carboxylate salt and, upon acidification with 1% aqueous hydrochloric acid, produced the aromatic carboxyl functionalized polystyrene derivative (2). The results of the quantitative formation of aromatic carboxyl functionalized polystyrenes in bulk and solution are outlined in Table 1.

**Scheme 1. Synthetic pathway for the \( \alpha \)-bromo-\( \beta \)-toluic acid initiated polymerization of styrene in the presence of CuBr/bpy catalyst in diphenyl ether at 130 °C.**

**Table 1. Characterization of the aromatic carboxyl chain-end functionalized polymers (2)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>( M_\text{SEC} )</th>
<th>( M_\text{NP} )</th>
<th>( M_\text{w}/M_\text{N} )</th>
<th>( M_\text{N,titration} )</th>
<th>( I_\text{eff} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^{c})</td>
<td>2200</td>
<td>2500</td>
<td>1.22</td>
<td>2500</td>
<td>0.87</td>
</tr>
<tr>
<td>2(^{d})</td>
<td>3160</td>
<td>3340</td>
<td>1.34</td>
<td>3320</td>
<td>0.94</td>
</tr>
<tr>
<td>3(^{e})</td>
<td>5970</td>
<td>6000</td>
<td>1.33</td>
<td>5900</td>
<td>0.99</td>
</tr>
<tr>
<td>4(^{f})</td>
<td>2589</td>
<td>2594</td>
<td>1.40</td>
<td>2549</td>
<td>0.99</td>
</tr>
<tr>
<td>5(^{g})</td>
<td>25890</td>
<td>25937</td>
<td>1.30</td>
<td>25494</td>
<td>0.99</td>
</tr>
</tbody>
</table>

\(^{a}\) Polymization of styrene initiated by \( \alpha \)-bromo-\( \beta \)-toluic acid in the presence of CuBr and 2,2'-bipyridyl catalyst system at 130 °C for 6 h.

\(^{b}\) Number average molecular weight in g mol\(^{-1}\).

\(^{c}\) Bulk polymerization: [CuBr]0:[1]0:[Bpy]0 = 1.56 mol l\(^{-1}\):0.29 mol l\(^{-1}\):0.65 mol l\(^{-1}\).

\(^{d}\) Solution polymerization: [CuBr]0:[1]0:[Bpy]0 = 1.18 mol l\(^{-1}\):0.18 mol l\(^{-1}\):0.53 mol l\(^{-1}\) in diphenyl ether (5 ml).

\(^{e}\) Polymerization of styrene initiated by \( \alpha \)-bromo-\( \beta \)-toluic acid in the presence of CuBr and 2,2'-bipyridyl catalyst system at 130 °C for 6 h.

\(^{f}\) Number average molecular weight in g mol\(^{-1}\).

\(^{g}\) Solution polymerization: [CuBr]0:[1]0:[Bpy]0 = 1.18 mol l\(^{-1}\):0.18 mol l\(^{-1}\):0.53 mol l\(^{-1}\) in diphenyl ether (5 ml).

\(^{h}\) Bulk polymerization: [CuBr]0:[1]0:[Bpy]0 = 0.11 mol l\(^{-1}\):0.05 mol l\(^{-1}\):0.11 mol l\(^{-1}\).

\(^{i}\) Solution polymerization: [CuBr]0:[1]0:[Bpy]0 = 0.072 mol l\(^{-1}\):0.032 mol l\(^{-1}\):0.11 mol l\(^{-1}\).
spot on the chromatogram, which corresponds to the formation of aromatic carboxyl functionalized polymer in quantitative yield. The size exclusion chromatographic (SEC) analysis of the aromatic carboxyl functionalized polystyrene (2) shows a monomodal molecular weight distribution (Fig 1) with $M_w/M_n = 1.22$ and $M_n = 3040$ g mol$^{-1}$. The result obtained from SEC analysis is consistent with the theoretical $M_{n,th}$ value of 2917 g mol$^{-1}$ for 85% monomer conversion as calculated according to eqn (1), where $[M]_0$ and $[R−X]_0$ represent the initial concentration of the monomer and the initial concentration of initiator, respectively, with $(MW)_0$ and $MW_{\text{init}}$ representing the molecular weight of the monomer and initiator, respectively.

$$M_{n,th} = ([M]_0/[R−X]_0) \times (MW)_0 \times \%\text{Conversion}/100 + MW_{\text{init}}$$  \hspace{1cm} (1)

The FTIR spectrum (Fig 2) of the carboxylated polystyrene (2), obtained after acidification of the copper carboxylate derivative, exhibits a carbonyl group absorption band at 1689 cm$^{-1}$, consistent with the incorporation of the initiator fragment into the functionalized polymer. The $^{13}$C NMR spectrum of the carboxylated polystyrene (Fig 3) shows a resonance at 171.6 ppm, which indicates the incorporation of the aromatic carboxyl functional group into the polymer chain. Potentiometric titration measurements of the carboxyl functionalized polymer with standardized sodium hydroxide indicate the quantitative incorporation of the carboxylic acid group into the polymer chain-end and the $M_n$ value of 3317 g mol$^{-1}$ obtained is in good agreement with the SEC measurements ($M_n = 3040$ g mol$^{-1}$) and elemental analysis data ($M_n = 3022$ g mol$^{-1}$).

$\alpha$-Bromo-$p$-toluic acid is an effective initiator for the ARTP of styrene. The acid functionality does not totally deactivate the catalyst. However, the acid functionality does cause a slight increase in the observed number average molecular weight, which indicates a decrease in initiator efficiency ($I_{\text{eff}} = M_{n,th}/M_{n,\text{SEC}} = 0.95$). The decrease in initiator efficiency can be ascribed to partial complexation of (1) with copper, which thereby reduces the concentration of active initiator present.

**Polymerization kinetics**

The solution ATRP of styrene was initiated with three different concentrations of $\alpha$-bromo-$p$-toluic acid (1) relative to styrene in the presence of CuBr/bpy catalyst in diphenyl ether at 130°C, and the reactions proceeded under heterogeneous conditions. The ratio of the concentration of monomer to initiator affects the rate of polymerization of styrene. At lower $[M]_0/[1]_0$ ratio, the reaction was the fastest and 95% monomer conversion was reached in 4h (Fig 4). When the $[M]_0/[1]_0$ ratio was increased to 100, monomer conversion with time decreased dramatically and a retardation in the reaction was observed at higher $[M]_0/[1]_0$ ratios. The number average molecular weight increased with conversion suggesting that no significant termination reactions were present once the initiation step was complete (Fig 5). Functionalized polymers with polydispersity ranging from 1.1 to 1.23 were obtained, indicating a fast initiation process.

![Figure 1. Size exclusion chromatogram of aromatic carboxyl functionalized polystyrene (2).](image-url)
which involves rapid equilibrium exchange between active and dormant species during polymerization. However, the observed number average molecular weight was consistently lower than the theoretical number average molecular weight values throughout the polymerization.

The first order kinetic plots of \( \ln([M_0]/[M]) \) versus time for the ATRP of styrene initiated by (1) are shown in Fig 6. The linear kinetic plots of polymerization obtained indicate that fast initiation has occurred and that a constant number of propagating species were generated throughout the polymerization. At the lower \( [M_0]/[I]_0 \) ratio, the reaction rate was the fastest and the reaction rate dropped significantly with increasing 

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**Figure 2.** FTIR spectrum of aromatic carboxyl functionalized polystyrene (2).

**Figure 3.** \( ^{13}C \) NMR spectrum of aromatic carboxyl functionalized polystyrene (2).
monomer concentration for the reaction \([\text{CuBr}]:[1] = 1\). However, when \([M]/[I]_0 = 100\) with the addition of 2 mol equivalents of CuBr relative to initiator (polymerization D), no significant effect on the rate of polymerization of styrene was observed compared to polymerization B where equimolar amounts of CuBr and (1) were used. Moreover, the addition of 3 mol equivalents of CuBr relative to initiator (polymerization E) led to a dramatic retardation effect in the polymerization rate (relative to polymerization B) with the formation polymers having somewhat higher polydispersity in the range 1.16–1.23, suggesting complexation of the copper(I) bromide with the acid functionality of (1), ie a decrease in initiator efficiency.

Experimental results indicate that (1) is a good initiator for the solution ATRP of styrene, and initiator efficiency greater than 0.94 is obtained for most polymerization reactions. The slightly reduced initiator efficiency suggests that complexation of the acid functionality of the functionalized initiator with copper(I) bromide occurs, even at low concentrations, rendering the copper salt–ligand catalyst complex inefficient. The quantitative incorporation of initiator fragment into the polymer chain-end in the ATRP of styrene and control of the major polymer properties number average molecular weight and polydispersity are attributed to the more efficient and rapid reaction of the benzyl bromide derivative with copper bromide–dipyridyl complex to facilitate rapid initiation of polymerization. However, complexation does occur between the copper ions and the \(\alpha\)-bromo-\(p\)-toluic acid initiator fragment of the functionalized polymer chain to form copper carboxylates, because the functionalized polymer was isolated as the copper carboxylate salt, which upon acidification produced the aromatic carboxyl polystyrene derivative.

**CONCLUSIONS**

The \(\alpha\)-bromo-\(p\)-toluic acid initiated polymerization of styrene in the presence of copper(I) bromide and 2,2’-bipyridyl in diphenyl ether produces quantitative yields of the corresponding aromatic carboxyl functionalized polystyrene. The polymerization is com-

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**Figure 4.** Plot of percentage monomer conversion versus time for the \(\alpha\)-bromo-\(p\)-toluic acid initiated polymerization of styrene in the presence of CuBr/bpy catalyst in diphenyl ether at 130°C: curve A, \([\text{Styrene}]_0 = 4.37 \text{ mol l}^{-1}, [1]_0 = [\text{CuBr}]_0 = 0.085 \text{ mol l}^{-1}\), \([\text{Bpy}]_0 = 0.175 \text{ mol l}^{-1}\); curve B, \([\text{Styrene}]_0 = 4.37 \text{ mol l}^{-1}, [\text{CuBr}]_0 = 0.045 \text{ mol l}^{-1}, [\text{Bpy}]_0 = 0.175 \text{ mol l}^{-1}\); curve C, \([\text{Styrene}]_0 = 4.37 \text{ mol l}^{-1}, [\text{CuBr}]_0 = 0.085 \text{ mol l}^{-1}, [\text{Bpy}]_0 = 0.045 \text{ mol l}^{-1}\).

**Figure 5.** \(M_n\) versus percentage monomer conversion data (filled shapes and crosses) and \(M_w/M_n\) versus percentage conversion data (corresponding open shapes and crosses) for the \(\alpha\)-bromo-\(p\)-toluic acid initiated polymerization of styrene in the presence of CuBr/bpy catalyst in diphenyl ether at 130°C: curve A, \([\text{Styrene}]_0 = 4.37 \text{ mol l}^{-1}\), \([1]_0 = [\text{CuBr}]_0 = 0.085 \text{ mol l}^{-1}\), \([\text{Bpy}]_0 = 0.175 \text{ mol l}^{-1}\); curve B, \([\text{Styrene}]_0 = 4.37 \text{ mol l}^{-1}, [1]_0 = [\text{CuBr}]_0 = 0.045 \text{ mol l}^{-1}\), \([\text{Bpy}]_0 = 0.175 \text{ mol l}^{-1}\); curve C, \([\text{Styrene}]_0 = 4.37 \text{ mol l}^{-1}, [1]_0 = [\text{CuBr}]_0 = 0.085 \text{ mol l}^{-1}\), \([\text{Bpy}]_0 = 0.045 \text{ mol l}^{-1}\); curve D, \([\text{Styrene}]_0 = 4.37 \text{ mol l}^{-1}, [1]_0 = [\text{CuBr}]_0 = 0.045 \text{ mol l}^{-1}\), \([\text{Bpy}]_0 = 0.175 \text{ mol l}^{-1}\); curve E, \([\text{Styrene}]_0 = 4.37 \text{ mol l}^{-1}\), \([1]_0 = [\text{CuBr}]_0 = 0.045 \text{ mol l}^{-1}\), \([\text{Bpy}]_0 = 0.085 \text{ mol l}^{-1}\), \([\text{Bpy}]_0 = 0.13\).

**Figure 6.** First order kinetic plots for the \(\alpha\)-bromo-\(p\)-toluic acid initiated polymerization of styrene in the presence of CuBr/bpy catalyst in diphenyl ether at 130°C: curve A, \([\text{Styrene}]_0 = 4.37 \text{ mol l}^{-1}\), \([1]_0 = [\text{CuBr}]_0 = 0.085 \text{ mol l}^{-1}\), \([\text{Bpy}]_0 = 0.175 \text{ mol l}^{-1}\); curve B, \([\text{Styrene}]_0 = 4.37 \text{ mol l}^{-1}, [1]_0 = [\text{CuBr}]_0 = 0.045 \text{ mol l}^{-1}\), \([\text{Bpy}]_0 = 0.175 \text{ mol l}^{-1}\); curve C, \([\text{Styrene}]_0 = 4.37 \text{ mol l}^{-1}, [1]_0 = [\text{CuBr}]_0 = 0.085 \text{ mol l}^{-1}\), \([\text{Bpy}]_0 = 0.045 \text{ mol l}^{-1}\); curve D, \([\text{Styrene}]_0 = 4.37 \text{ mol l}^{-1}, [1]_0 = [\text{CuBr}]_0 = 0.045 \text{ mol l}^{-1}\), \([\text{Bpy}]_0 = 0.175 \text{ mol l}^{-1}\); curve E, \([\text{Styrene}]_0 = 4.37 \text{ mol l}^{-1}, [1]_0 = [\text{CuBr}]_0 = 0.045 \text{ mol l}^{-1}\), \([\text{CuBr}]_0 = 0.13, [\text{Bpy}]_0 = 0.085 \text{ mol l}^{-1}\).
plete within several hours and proceeds via a living, controlled route to afford quantitative yields of the corresponding aromatic carboxyl functionalized polymers with predictable molecular weights ($M_n = 1600 – 25,900$ g mol$^{-1}$), narrow molecular weight distribution ($M_w / M_n = 1.1 – 1.40$) and initiator efficiency above 0.94. The polymerization process was monitored by gas chromatographic analysis. The functionalized polymers were characterized by thin layer chromatography, size exclusion chromatography, spectroscopy, potentiometry and elemental analysis. All polymer characterization data are consistent with the quantitative incorporation of the aromatic carboxyl group into the polymer chain-end.

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