Synthesis of amphiphilic copolymers by ATRP initiated with a bifunctional initiator containing trichloromethyl groups

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Abstract

Bifunctional polystyrene macroinitiators, having various molecular weights, were prepared by atom transfer radical polymerization (ATRP), initiated with bifunctional initiator 1,3-bis{1-methyl-1[(2,2,2-trichloroethoxy) carbonyl-amino]ethyl}benzene in conjunction with CuCl catalyst and polyamine ligands. These macroinitiators were subsequently used for ATRP of tert-butyl acrylate (t-BuA), giving BAB triblocks poly[(t-BuA)-b-(Sty)-b-(t-BuA)] as precursors of amphiphilic copolymers. Both the polymerization steps proceeded as controlled processes with linear semi-logarithmic conversion plots and lengths of the blocks following theoretical predictions. Hydrolysis of outer poly(t-BuA) blocks led to triblock copolymers with the central polystyrene block and outer blocks of poly(acrylic acid), the molecular weights of which ranged from ca. $5 \times 10^3$ to almost $1 \times 10^5$ Da.

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1. Introduction

A three-component initiating system for atom transfer radical polymerization (ATRP) contains halide-type true initiator, catalyst – a transition metal salt in the lower oxidation state, and a complexing ligand, based on amine-type or organophosphorus compounds [1,2]. In addition to alkyl or aryl halides, esters of haloorganic acids, also polyhalogenated compounds of the general formula R–CX₃ can serve as ATRP initiators, in which –R can be hydrogen, halogen, or various organic substituents. However, due to their chemical structure these compounds can, at least theoretically, act as bifunctional initiators. Initiating behavior of various R–CCl₃ in combination with a CuCl catalyst and a bipyridine (bpy) ligand was studied in detail from both the kinetic and mechanistic point of view by Destarac et al. [3]. It was shown that these initiators can be, with respect to their initiating efficiency, divided into two basic groups: (i) those, containing activating electron-withdrawing group adjacent to the –CCl₃ (e.g., esters of trichloroacetic acid or (dichloromethyl)benzene) and (ii) those, in which...
–R is alkyl, not activating alkylhalide group (e.g., 1,1,1-trichlorononane). Kinetic studies documented that the polymerization rate of styrene depends on the type of the R-substituent. Specifically, when initiated with activated initiators, the polymerization proceeds with a higher rate when initiated with a non-activated type. Moreover, size exclusion chromatography (SEC) and nuclear magnetic resonance (NMR) studies showed that non-activated initiators are clearly monofunctional, whereas some of the activated types can behave as bifunctional. ATRP of MMA initiated with R–CCl₃ compounds under the same catalysis was presented in another work of the same authors [4], offering similar conclusions. Moreover, it was established here that the number average molecular weight (Mₙ) of PMMA, formed in polymerization initiated with CCl₄ does not increase linearly with monomer conversion. This behavior could be caused by formation of branches, initiated with a chlorine atom from the central CCl₂ group. However, model polymerizations initiated with Cl₂CHCH₂OH or CH₃CCl₂CH₃ did not verify this idea because the process was very slow. The non-linearity of the dependence of Mₙ on monomer conversion was explained by a possible β-scission of the chains containing the central CCl₂ group, leading to a non-active polymer and a new macroradical. However, when initiator with non-activated trichloromethyl groups is used instead of CCl₄, β-scission of the chains was not detected as has been shown in our recent work [5]. In addition, the functionality of polyhalogenated macroinitiators can also depend on the type of monomer, as has been documented by Hoecker et al. in polymerizations of styrene and MMA, initiated with (dichloromethyl)benzene [6].

We have synthesized recently a bifunctional ATRP initiator, 1,3-bis{1-methyl-1[(2,2,2-trichloroethoxy) carbonylamino]ethyl}benzene with two trichloromethyl groups, by condensation of 2,2,2-trichloroethan-1-ol and aromatic diisocyanate 1,3-bis[1-isocyanato-1-methylethyl]benzene (BI-1, Scheme 1) [7]. This compound was successfully used in combination with a CuCl catalyst and amine-type ligands in controlled ATRP synthesis of PMMA and PMMA/t-BuA block copolymers [5] with tailorable block lengths. Here, we present an application of this initiator in preparing poly[(tert-butyl acrylate)-block-styrene-block-(tert-butyl acrylate)] (poly[(t-BuA)-b-(Sty)-b-(t-BuA)]) and poly(tert-butyl acrylate)-block-[styrene-co-(2-hydroxyethyl methacrylate)]-block-(tert-butyl acrylate) (poly[(t-BuA)-b-(Sty-co-HEMA)-b-(t-BuA)]) triblock copolymers and their corresponding amphiphilic analogues, which possess outer poly(acrylic acid) blocks.

2. Experimental

2.1. Materials

Styrene (Sty, >99%, Fluka), tert-butyl acrylate (t-BuA, >98%, Fluka) were distilled from calcium hydride under reduced pressure and stored in a freezer under argon atmosphere. 2-Hydroxyethyl methacrylate (HEMA, >99%, Aldrich) was passed through a column filled with alumina in order to remove inhibitor and stored under argon in freezer. Toluene, acetone, and dichloromethane (>99%, Fluka) were distilled from calcium hydride and stored under argon at room temperature. 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 97%, Aldrich), N,N,N0,N00-pentamethyldiethylene-triamine (PMDETA, 99%, Aldrich), copper (Cu, powder 200 mesh, >98%, Aldrich), trifluoroacetic acid (TFA, >99%, Aldrich), 3-isopropenyl-α,α-dimethylbenzyl isocyanate (>95%, Aldrich), and dibutyltin dilaurate (DBTDL, >95%, Aldrich) were used as received. CuCl (>99%, Aldrich) was purified by washing with glacial acetic acid, absolute ethanol, and finally with diethyl ether. The bifunctional initiator containing trichloromethyl groups (BI-1) was synthesized in the same way as described earlier by Toman et al. [7].

2.2. Polymer synthesis

2.2.1. Polystyrene homopolymers (1A) and random copolymers with HEMA (1B)

In a typical experiment, CuCl (0.1368 g, 1.05 mmol) and bifunctional initiator BI-1 (1.1187 g, 2.09 mmol) were added to a flask, equipped with a magnetic stirring bar. After sealing with a three-way stopcock, the flask was degassed and backfilled with argon three times. Subsequently, styrene (12 ml, 104.73 mmol) and toluene (11 ml) as a
solvent, were added. Then, the complexing ligand, HMTETA (0.29 ml, 1.05 mmol) or PMDETA (0.22 ml, 1.05 mmol), was added and the solution was stirred until the complex was formed. The mixture was frozen in dry-ice ethanol bath and degassed by three freeze–pump–thaw cycles. The flask was subsequently placed in an oil bath and stirred at 110 °C for 10 h. Then, the reaction was quenched by intensive cooling and diluted with tetrahydrofuran (THF). This crude reaction mixture was analyzed by gas chromatography (GC) and SEC; the formed polymer was recovered by precipitation in acidic methanol/water mixture = 80/20 (v/v) and dried in vacuum at 40 °C to constant weight.

Random copolymers of styrene with HEMA (mole ratio 1:50) were prepared by following the same polymerization procedure.

2.2.2. Synthesis of poly[(t-BuA)-b-(Sty)-b-(t-BuA)] (2A) and poly[(t-BuA)-b-(Sty-coHEMA)-b-(t-BuA)](2B) triblock copolymers

A reaction flask, equipped with a three-way stop-cock and a magnetic stirring bar was charged with macroinitiator 1A or 1B (1.0068 g, 0.205 mmol, $M_n = 4900$, $M_w/M_n = 1.19$), CuCl (20.27 mg, 0.205 mmol), copper powder (200 mesh, 39.04 mg, 0.614 mmol), and flushed with argon. The flask was then evacuated and backfilled with argon three times. Afterwards, t-BuA (3 ml, 20.48 mmol), PMDETA (42.8 µl, 0.205 mmol), and dried acetone (2 ml) were added with gas-tight syringes. The reaction mixture was repeatedly frozen in dry-ice/ethanol bath and backfilled with argon for 30 min in order to remove oxygen. The polymerization was carried in oil bath at 70 °C for 16 h. Quenching, isolation, and analysis of such prepared block copolymers followed the same procedure as that for polystyrene homopolymers.

2.2.3. Modification of 2B with 3-isopropenyl-α,α-dimethylbenzyl isocyanate (3B)

A mixture of 2B copolymer containing 2-hydroxyethyl groups from the HEMA units (12.25 g, $2.4 \times 10^{-6}$ mol of OH groups), and 3-isopropenyl-α,α-dimethylbenzyl isocyanate (50 µl, 0.025 mmol) in dichloromethane (50 ml) was treated with a catalytic amount of dibutyltin dilaurate. The solution was stirred at ambient temperature for 24 h. The reaction mixture was repeatedly frozen in dry-ice/ethanol bath and backfilled with argon for 30 min in order to remove oxygen. The polymerization was carried in oil bath at 70 °C for 16 h. Quenching, isolation, and analysis of such prepared block copolymers followed the same procedure as that for polystyrene homopolymers.

2.2.4. Hydrolysis of 2A and 3B

A round-bottom flask fitted with magnetic stirrer was charged with 2A or 3B (10 g, 72.44 mmol of tert-butyl ester groups), followed by dichloromethane (50 ml). The mixture was subsequently stirred for 10 min at room temperature in order to dissolve the polymer. Trifluoroacetic acid (26.9 ml, 0.36 mol, i.e., fivefold excess over the tert-butoxy groups) was then added and the mixture was stirred at room temperature for 24 h. The solvent and unreacted trifluoroacetic acid were then removed from the resulting heterogenous mixture by decantation, and the residual solid product was washed with dichloromethane three-times followed by drying under vacuum at room temperature to constant weight.

2.3. Measurements

2.3.1. Size exclusion chromatography (SEC)

All polymers were characterized by SEC (Labora, Czech Rep.) in THF at room temperature at a flow rate of 1 ml/min using a set of two PSS-SDV columns (5 µm; $10^3$ and $10^5$ Å) (PSS, Germany), equipped with RI and UV detectors. Polystyrene standards and the Mark–Houwink constants for the PS/THF system ($K = 1.17 \times 10^{-4}$ mL g$^{-1}$, $a = 0.717$) were used to establish the number average molecular weights ($M_n$) and molecular weight distributions (MWD). Obviously, for block copolymers only their apparent $M_n$ values were obtained in this way.

2.3.2. Nuclear magnetic resonance (NMR)

$^1$H NMR spectra of 10% (w/w) solutions in CDCl$_3$ or DMSO-$d_6$ were measured at 330 K with a Bruker Avance DPX300 spectrometer at 300.13 and 75.45 MHz resonance frequency, respectively. The spectra were measured in a quadrature mode. For $^1$H NMR, 32 k points were collected in 32 scans, the repetition time being 12 s. The integral intensities of characteristic signals were measured using the software supplied with the NMR spectrometer.

3. Results

3.1. Homopolymerization of styrene

Styrene was polymerized in toluene with a CuCl/HMTETA (or PMDETA) catalyst system and a bifunctional initiator with 2,2,2-trichloroethyl functional groups (BI-1) at 110 °C. The choice of
a suitable catalyst/ligand system is a key parameter in establishing the dynamic equilibrium between the dormant and active species as the basic conditions for well-controlled ATRP [8]. Malinowska et al. [5] reported that ATRP of MMA initiated with the abovementioned initiator and catalysed with the HMTETA/CuCl was well-controlled, which indicates a high activity of the catalytic complex [9]. The results from the polymerization of styrene catalyzed with the CuCl/HMTETA or CuCl/PMDETA complexes are summarized in Table 1. The experiments were performed using various catalyst concentrations (with respect to that of the initiator), depending on the Sty/BI-1 mole ratio. If this ratio was low, i.e., 50 (Runs 1 and 2) and the polymerizations took place in toluene; better results were obtained if the concentrations of both the CuCl and HMTETA equalled one half of the initiator content (Run 1). The dependence of ln[M]₀/[M] on the reaction time was linear (cf. Fig. 1), indicating a constant equilibrium concentration of active radicals and, therefore, a controlled process. However, changing the BI-1/CuCl/HMTETA mole ratio to 1/1/1 (Run 2) resulted in the product with a broad MWD. Also, the dependence of ln[M]₀/[M] on the reaction time was curved upward in this case (cf. Fig. 1). Obviously, the lower catalyst concentration favorably lowers the concentration of active radicals in the system. Nevertheless, higher concentrations of a catalyst and ligand, is recommended for synthesis of polystyrenes with higher molecular weights (Runs 3–6). As can be seen from these results, Mₐ of the prepared polymers follows the theoretical values in the range of almost two orders of magnitude.

Bulk polymerizations, under otherwise the same conditions, proceed also to high conversions (Runs 4–6). However, the MWDs of the polymers are slightly broadened and their molecular weights do not exactly follow theoretical predictions; in particular, if the monomer/initiator mole ratio is as high as 500 or even 1000. It can be assumed, that termination reactions are non-negligible under these conditions.

In further experiments (Runs 7–12), the PMDETA ligand was tested under similar reaction conditions.

Table 1

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Ligand</th>
<th>Feed composition⁶</th>
<th>Reaction time (h)</th>
<th>GC conversion (%)</th>
<th>Mₙ,calc</th>
<th>SEC</th>
<th>Mₙ</th>
<th>Mₘ/Mₙ</th>
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<td>1</td>
<td>HMTETA</td>
<td>1:0.5:0:5:50⁷</td>
<td>9</td>
<td>76.64</td>
<td>4400</td>
<td>4600</td>
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<td>2</td>
<td></td>
<td>1:1:1:50⁸</td>
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<td>93700</td>
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<td>16200</td>
<td>1.24</td>
<td></td>
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<tr>
<td>12</td>
<td></td>
<td>1:2:2:500⁹</td>
<td>18</td>
<td>84.80</td>
<td>44100</td>
<td>41400</td>
<td>1.23</td>
<td></td>
</tr>
</tbody>
</table>

* BI-1:CuCl:ligand:Sty mole ratio.
* Sty/toluene = 55/45 v/v.
* Bulk polymerization.
* Sty/toluene = 68/32 v/v.
With a low catalyst concentration and a low excess of styrene over the initiator, i.e., for the BI-1:CuCl:ligand:Sty mole ratio equal to 1:0.5:0.5:50, the polymerization in toluene proceeds slowly resulting in a product with a narrow MWD (Run 7). An increase in the concentration of the catalyst components (BI-1:CuCl:PMDETA = 1:1:1) led to a higher reaction rate in toluene as well as in the bulk (Runs 8 and 9). Moreover, the linear dependence of $\ln([M]_0/[M])$ on the reaction time indicated a well-controlled polymerization under these conditions (cf. Fig. 2). Also, experiments with a higher Sty/initiator mole ratio (Runs 10–12) resulted in narrow MWD products whose molecular weights corresponded to the theoretical values. Thus, PMDETA is a more convenient ligand in this polymerization, leading to a controlled process under a wide range of concentration conditions. This can probably be due to a lower redox potential of the CuCl/PMDETA complex, compared with CuCl/HMTETA [10].

### 3.2. Block copolymers

Since polystyrenes prepared by ATRP initiated with the bifunctional polyhalogenated initiator BI-1 mentioned above, are linear and symmetric, having C–Cl bonds at both ends, they can be used

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Feed composition a</th>
<th>GC conversion (%)</th>
<th>Reaction time (h)</th>
<th>$M_n,\text{calc}$</th>
<th>$M_n,\text{NMR}$</th>
<th>$M_n,\text{SEC}$</th>
<th>$M_w/M_n$</th>
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<td>17</td>
<td>8100</td>
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<td>17</td>
<td>16600</td>
<td>17400</td>
<td>18200</td>
<td>1.22</td>
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<td>15</td>
<td>1:1:3:1:50 d</td>
<td>49.97</td>
<td>17</td>
<td>11300</td>
<td>12800</td>
<td>12500</td>
<td>1.13</td>
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<tr>
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<td>1:1:3:1:100 e</td>
<td>95.80</td>
<td>8</td>
<td>11000</td>
<td>15900</td>
<td>18400</td>
<td>1.32</td>
</tr>
<tr>
<td>17</td>
<td>1:1:3:1:200 f</td>
<td>93.20</td>
<td>11.5</td>
<td>16500</td>
<td>18600</td>
<td>19100</td>
<td>1.17</td>
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<tr>
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<td>29200</td>
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<td>30500</td>
<td>1.22</td>
</tr>
<tr>
<td>19</td>
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<td>18</td>
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<td>41600</td>
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<tr>
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<td>98700</td>
<td>92300</td>
<td>73600</td>
<td>1.30</td>
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</table>

Note: For Run 13–19, PSty-macro with: $M_{n,\text{SEC}} = 4900$, $M_w/M_n = 1.19$ was used. For Runs 20–21, PSty-macro with: $M_{n,\text{SEC}} = 5000$, $M_w/M_n = 1.22$ was used.

- a Mole ratio.
- b PSty-macro:CuCl:PMDETA:tert-BuA, 50% (v/v) DMF.
- c PSty-macro:CuCl:PMDETA:tert-BuA, 50% (v/v) anisole.
- d PSty-macro:CuCl:PMDETA:tert-BuA, 50% (v/v) acetone.
- e PSty-macro:CuCl:Cu:PMDETA:tert-BuA, 40% (v/v) acetonitrile.
- f PSty-macro:CuCl:Cu:PMDETA:tert-BuA, 60% (v/v) acetone.
as α,ω-bifunctional macroinitiators (PSty-macro) for ATRP of other monomers.

As documented recently, ATRP of tert-butyl acrylate proceeds in a controlled manner under CuBr/PMDETA catalysis in polar solvents such as DMF, acetone and 1,4-dimethoxybenzene [11], or anisole [12]. The results of our experiments, performed at 70 °C in various solvents, are summarized in Table 2. The polymerization of t-BuA in DMF (Run 13) proceeds slowly, reaching only 25% conversion after 17 h. Moreover, the $M_n$ of the product is much higher than its theoretical value and the MWD is rather broad. This is in contrast with results by Davis and Matyjaszewski which described DMF as a good solvent for ATRP of t-BuA [11]. Perceptibly better results were obtained when anisole or acetone were used as solvents (Runs 14 and 15). Polymerization in anisole reached almost quantitative conversion (91%) after 17 h, $M_n$ of the prepared polymer corresponds to the expected value and also MWD is acceptably narrow. Polymerization in acetone (Run 15) is faster than that in DMF, but slower than that in anisole; the monomer conversion reaches nearly 50% within the same time interval. The molecular weight of the product is in a good agreement with the theoretical value and its PDI is even lower than that of the polymer prepared in anisole even in the presence of Cu0 powder (Run 17). Thus, under these reaction conditions, the lengths of the poly(t-BuA) blocks in copolymers can be controlled stoichiometrically over a wide range, as documented by Runs 16–21. Both of these solvents were already successfully used for ATRP of t-BuA [11,12], however, we observed lower polymerization rate. The differences can originate from different starting monomer concentrations and different catalysts (CuCl vs. CuBr).

The semilogarithmic plot of monomer consumption vs. time is also linear, suggesting a constant concentration of active radicals during the polymerization (cf. Fig. 3, Run 16 in Table 2). In all experiments listed in Table 2, there were no detectable amounts of unreacted macroinitiator in resulting block copolymers. SEC eluograms of macroinitiators and the corresponding block copolymers of Runs 15 and 21 (cf. Figs. 4 and 5) are symmetric and narrow, without a hint of bimodality or even tailing.

3.3. Hydrolysis of block copolymers

For hydrolysis of the ester groups of the poly(t-BuA) blocks of the copolymers, trimethylsilyl iodide (TMSI) was proposed as an effective dealkylation reagent under neutral and mild conditions [13]. Thus, the modified Olah’s method was applied to hydrolysis of the copolymer 2A and TMSI was generated in situ by a reaction of trimethylsilyl chloride (TMSCl) and sodium iodide (NaI). However, the final product, obtained after a hydrolysis with HCl, remained brown colored regardless of the repeated treatment with sodium thiosulfate. This is why this method was abandoned.

Consequently, trifluoroacetic acid (TFA) in non-polar aprotic solvent such as CH2Cl2 under mild conditions was used, according to literature [14]. The resulting amphiphilic block copolymers then precipitated from the solution mixture during hydrolysis and could be easily separated and purified by decantation. The products were characterized by 1H NMR in DMSO-d6 see Fig. 6. The peak corresponding to methyl protons in t-butyl ester groups (1.43 ppm) disappeared after hydrolysis, whereas the peak at 9.53 ppm, typical for a
hydroxyl group, arose, documenting complete hydrolysis of the ester.

The bifunctional initiator (BI-1), incorporated in the chains of both the polystyrene macroinitiators and block copolymers, contains urethane bonds (cf. Scheme 1), which could also undergo hydrolysis under alkaline or acid conditions [15]. Thus, it was necessary to verify its stability in a solution of TFA in dichloromethane used for hydrolysis of tert-buty1 ester groups. The test was performed with a polystyrene macroinitiator, ($M_{n,SEC} = 41400$, Run 12 in Table 1), which was treated with a mixture of TFA and dichloromethane, then isolated and again analyzed by SEC (cf. Fig. 7). Both the traces have the same shape and position, without a hint of low-molecular weight shoulder which would appear as a consequence of hydrolysis of the urethane bond in polystyrene chains. Therefore, TFA in CH$_2$Cl$_2$ is a suitable agent for hydrolysis of tert-butyl ester groups as it produces no scission of urethane bonds in the polymer chains.

Fig. 6. $^1$H NMR spectra of: (A) poly[(t-BuA)-b-(Sty)-b-(t-BuA)]; (B) poly[(AA)-b-(Sty)-b-(AA)].

Fig. 7. SEC eluograms of the polystyrene macroinitiator ($M_{n,SEC} = 41400$, $M_w/M_n = 1.23$) before (1) and after (2) hydrolysis.
Scheme 2.

\[(1B)\] $t$-BuA, CuCl/Cl/PMDTA

\[70\,^\circ\text{C};\,16\,\text{h};\,\text{acetone}=60\,\%\,(v/v)\]

\[(2B)\]

\[(3B)\] 3-isopropenyl-$\alpha,\alpha$-dimethylbenzyl isocyanate

DBTDL, RT, 24 h

\[(4B)\] TFA, RT, 24 h

Scheme 2.
Fig. 8. $^1$H NMR spectra of: (A) poly[(Sty)-co-(HEMA)]; (B) poly[(t-BuA)-b-(Sty-co-HEMA)-b-(t-BuA)]; (C) poly[(t-BuA)-b-(Sty-co-HEMA)-b-(t-BuA)] modified with vinyl double bonds.
3.4. Modification of block copolymers with vinyl double bonds

Amphiphilic block copolymers based on styrene and acrylic acid can be used, after neutralization of acid groups, as polymeric surfactants capable of stabilizing polymeric dispersions in emulsion polymerizations [16–18]. For better stabilizing efficiency, the hydrophobic block of the copolymer can be chemically anchored on a particle surface while the hydrophilic blocks extend into the aqueous phase and create a well-defined hydrophilic shell. In order to achieve this, it is suitable to introduce pendant vinyl double bonds on the hydrophobic block of the copolymer, which can subsequently copolymerize with monomer(s) present on any micellar surface [19,20].

To obtain such a “polymerizable” surfactant (cf. Scheme 2), we first prepared a styrene/HEMA random copolymer by ATRP of styrene with HEMA (mole ratio 1:50), initiated with BI-1 and catalyzed with the CuCl/PMDETA system under the same conditions as mentioned above (Run 8, cf. Table 1). The product (1B) was analyzed by SEC and $^1$H NMR: $M_n,NMR = 5100$, $M_n,calc = 5200$, $M_w/M_n = 1.23$; HEMA/Sty mole ratio ($\approx 1:56$) was established from integrated intensities of the methylene groups of the HEMA (4.3 ppm) units and the protons of aromatic rings of styrene (6.5–7.3 ppm) (cf. Fig. 8A). Further, this hydroxy-functionalized polystyrene was used as a macroinitiator for ATRP of $t$-BuA under the standard conditions presented above (Run 20, cf. Table 2). The mole ratio of $t$-BuA monomer to the poly[(Sty-co-HEMA)]

![Fig. 9. $^1$H NMR spectra poly[(Sty-co-(HEMA)] modified with vinyl double bonds, before (A) and after (B) hydrolysis.](image-url)
macroinitiator was equal to 500. SEC analysis of the resulting block copolymer (2B) (not shown) revealed a narrow MWD without a hint of bimodality or the presence of any unreacted macroinitiator. However, $^1$H NMR spectrum of the block copolymer 2B (cf. Fig. 8B) shows no signals of methylene protons at 4.3 ppm assigned to HEMA. This discrepancy can be explained by a very low concentration of HEMA ($3.6 \times 10^{-3}$ mol%) in the block copolymer chains with $M_n,\text{NMR} = 70100$, which is below the resolution limit of $^1$H NMR. The 2B copolymer then reacted with 3-isopropenyl-$\alpha,\alpha$-dimethylbenzyl isocyanate under DBTDL catalysis, which introduced double bonds onto the HEMA units. The missing signals at 5.0 and 5.3 ppm (the methylene protons) and at 2.13 ppm (the methyl protons from $\text{A}C(CH_3)$ groups) in the $^1$H NMR spectrum of the block copolymer 3B (cf. Fig. 8C) can also be interpreted in the same way as above. Finally, poly$(t$-BuA) block of this copolymer was hydrolyzed with TFA (see above), giving an amphiphilic triblock with pendant isopropenyl double bonds present on the lipophilic block (4B) (cf. Scheme 2).

Since the concentrations of the vinyl bonds and 2-hydroxyethyl groups in the final modified poly-[$(t$-BuA)$b$-$\text{Sty}$-$\text{co}$-HEMA]$b$-$$(t$-BuA)] were below the detection limit of $^1$H NMR, a separate test was performed with the poly[$(\text{Sty}$-$\text{co}$-HEMA)$] macroinitiator 1B mentioned above; HEMA/Sty mole ratio was 1:56, with $M_n,\text{NMR} = 5100$ and $M_w/M_n = 1.23$. This precursor was condensed with the unsaturated aromatic isocyanate in the same way as for copolymer 2B. The obtained modified macroinitiator was then analyzed by $^1$H NMR; the spectrum in Fig. 9A clearly indicates the presence of signals of both the methylene (5.0 and 5.3 ppm) and methyl protons (2.13 ppm), which arise from the $\text{A}C(CH_3)$ groups. The degree of functionalization of HEMA hydroxy groups with the isopropenyl double bonds was established from integrated intensities of the methylene groups of the HEMA (4.3 ppm) units and methylene protons of the isopropenyl groups. The mole ratio of isopropenyl groups to styrene units in the polymer was ca. 1:40, which was slightly higher than that for HEMA units (1:56) in the copolymer. This discrepancy

\[ \text{(A)} \quad \text{3-isopropenyl-$\alpha,\alpha$-dimethylbenzyl isocyanate} \quad \text{RT, 24 h, DBTDL} \]

\[ \text{(B)} \quad \text{3-isopropenyl-$\alpha,\alpha$-dimethylbenzyl isocyanate} \quad \text{RT, 24 h, DBTDL, Slow} \]

\[ \text{(C)} \]

Scheme 3.
likely originates from the formation of allophanate structures (cf. Scheme 3C) by the reaction of —NH— groups in urethane groups (cf. Scheme 3B) with the isocyanate, which was used in a tenfold molar excess with respect to hydroxy groups. Moreover, a long reaction time of the modification (see Experimental section) can also play a non-negligible role in this respect. This modified polystyrene macrorinitiator was also treated with TFA in order to verify hydrolytic stability of the urethane bond. The $^1$H NMR spectra, collected before (cf. Fig. 9A) and after (cf. Fig. 9B) the treatment, clearly show the same intensities of the signals of the isopropenyl protons (5.0; 5.3 and 2.13 ppm), thus indicating that scission of the urethane group does not take place to a detectable extent.

Since the modification of HEMA units in the random copolymers proceeds smoothly with high yields, one can speculate about the same behavior in the case of modification of high-molecular weigh block copolymers.

Stabilizing efficiency of the prepared amphiphilic triblock copolymer, functionalized with isopropenyl double bond was preliminarily tested in a simple emulsion polymerization of the Sty/BuA/HEMA monomer mixture under conventional conditions. The experiment, performed in the presence of rather low concentration of the surfactant (1–2 mol% with respect to the monomers) gave stable latex of the corresponding copolymer. Let’s note that the latex remains stable and without visible change of viscosity within more than two months. Of course, detailed independent study would be needed to optimize the emulsion polymerization system including structure, molecular parameters and concentration of the triblock copolymer; nevertheless, remarkable stabilizing effect of the amphiphilic triblock has been clearly indicated.

4. Conclusion

Bifunctional initiators with trichloromethyl active groups were successfully used to synthesize polystyrene homopolymers and a styrene/HEMA random copolymer using ATRP catalyzed with CuCl in the presence of amine-type ligands. With both the ligands, HMTETA or PMDETA, the ATRP proceeds in a ‘living’ manner, giving polystyrenes with narrow MWDs and $M_n$, which are near to the theoretical values. The molecular weight of polystyrenes can be controlled over more than two orders of magnitude while keeping MWDs narrow.

The polystyrenes thus prepared were then used as bifunctional macrorinitiators for the polymerization of t-BuA under CuCl/Cu/PMDETA catalysis, leading to corresponding triblock copolymers with variable block lengths. Polymerizations in acetone led to copolymers with the narrowest MWDs and predictable molecular weights.

The poly[(t-BuA)-b-(Sty)-b-(t-BuA)] copolymers thus synthesized were hydrolyzed using TFA in dichloromethane to yield corresponding amphiphilic block copolymers with outer poly(AA) blocks. The chosen method of hydrolysis could quantitatively and selectively convert the tert-butyl ester to carboxylic groups under mild conditions, as confirmed by SEC and $^1$H NMR.

The polystyrene macrorinitiator containing HEMA units can be modified, after the synthesis of block copolymers, by introducing the vinyl double bonds. Subsequent hydrolysis of the poly(t-BuA) blocks results in amphiphilic block copolymers containing polymerizable vinyl bonds in the hydrophobic polystyrene block. The amphiphilic block copolymers modified in this way can be used, after neutralization of poly(AA) blocks, as polymeric surfactants and steric stabilizers in emulsion polymerizations.

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