PSt-*b*-PU-*b*-PSt copolymers using tetraphenylethane-urethane macroinitiator through SARA ATRP

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Abstract. The course of supplemental activator and reducing agent (SARA) atom transfer radical polymerization (ATRP) has been presented in the presence of Cu⁰. The novelty of this work is that SARA ATRP has been used for the first time to synthesize polystyrene-*b*-polyurethane-*b*-polystyrene copolymers by using tetraphenylethane-urethane macroinitiator as transitional products reacting with styrene in the presence of Cu^{II}Br₂/TPMA catalyst complex. The influence of copper surface area on the polymerization was examined. It was confirmed that in all cases, both the molecular weight of resulting copolymer increases linearly with increasing conversion as well as the value of $\ln([M]_0/[M])$ as a function of polymerization time increases linearly. A successful formation of the urethane-styrene copolymers was confirmed by NMR spectral studies.

Keywords: polymer synthesis, molecular engineering, SARA ATRP, copolymers, polyurethanes, polystyrene

1. Introduction

Atom transfer radical polymerization (ATRP) is one of the most rapidly developing areas of polymer science, allowing to obtain effective control over molecular weights (MWs), narrow molecular weight distributions (MWDs), architectures, and well-defined compositions [1–9]. However, normal ATRP has one significant limitation – it requires a large amount of the catalyst, which is sensitive to air and other oxidant. In order to overcome this drawback, Matyjaszewski's group has developed an improved ATRP technique, known as supplemental activator and reducing agent (SARA) [10]. This method provides a continuously controlled polymerization with reduction of the amount of copper-based catalyst complex (<50 ppm) due to constant regeneration of the Cu^I activator species by reducing agent (zerovalent metal – Cu⁰), which compensates for any

loss of Cu^I by termination [11]. Lowering the concentration of the catalysts not only results in 'greener' polymerization processes but also allows for the synthesis of polymers with high MW and high chain-end functionality [12]. Moreover, SARA ATRP offers simple removal and reuse of unreacted solid Cu⁰, control of the polymerization rate by the amount of ligand and the surface area of Cu⁰ [13, 14].

SARA ATRP, has Cu^I/Cu^{II} reactions as the major activation/deactivation ones, with Cu⁰ acting as a supplemental activator of alkyl halides and a reducing agent for excess Cu^{II}, and limiting disproportionation of Cu^I (Figure 1) [15, 16].

Meanwhile, Percec group has proposed a single electron transfer living radical polymerization (SET-LRP) mechanism [18–22], which postulates Cu⁰ as the major activator of alkyl halides, Cu^{II} as the major deactivator and assumes that Cu^I not participating

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Figure 1. Mechanism of SARA ATRP. Line thickness denotes the contributions of the reactions (bold – major reactions, solid – contributing reactions, and dashed – negligible reactions) [17]

in activation reactions and instead undergoing very rapid disproportionation to Cu^0 and Cu^{I} [19]. Taking into account the Matyjaszewski's researches [17, 23, 24] it can be stated that the SARA ATRP mechanism is correct.

SARA ATRP/SET-LRP was successfully applied to relatively nonpolar monomers (e.g., styrene [25], butyl acrylate [26], methyl acrylate [14, 24, 26, 27], 2-(diisopropylamino) ethyl methacrylate [26, 28], methyl methacrylate [19, 26, 29]), as well as polar monomers (e.g., oligo(ethylene oxide) monomethyl ether acrylate [13], *N*-isopropylacrylamide [30]) for the preparation of a variety of polymeric materials with different structures and architectures, including homopolymers, and well-defined block copolymers.

However, tri-block copolymers have sparked much interest and their potential has been realized in many areas. These block copolymers have been used commercially as thermoplastic elastomers, adhesives, surfactants, hot-melt adhesives, blend compatibilizers, membranes, drug delivery polymers and biodegradable polymers [31]. Block copolymers are an interesting class of materials that possess different and often desirable properties compared to those of each individual homopolymer segments they are composed of [32]. As block length is playing a major role on the properties of the block copolymers, effective control of the block lengths is important and this can easily be achieved using different ATRP methods [31].

Bearing in mind the progress in application of the ATRP methods, it appears to be promising to use the SARA technique for obtaining urethane-styrene copolymers, which have been synthesized so far within a very limited scope by means of the ATRP classical mechanism [33, 34]. Therefore in this article, we have focused on the polymerization of styrene in the presence of tetraphenylethane-urethane macroinitiator (TPE-PU-TPE), $\text{Cu}^{\text{I}}\text{Br}_2$ as a catalyst, and

tris(2-pyridylmethyl)amine (TPMA) as a complexing agent. The resulting polystyrene-*b*-polyurethane-*b*-polystyrene (PSt-*b*-PU-*b*-PSt) tri-block copolymers obtained through SARA ATRP are reported now for the first time. It is also worth noticing that urethane-styrene copolymers are already commonly used as adhesives, emulsifiers, modifiers of surface properties and polymer blend compatibilizers [35, 36].

2. Experimental section

2.1. Materials

4,4'-Methylene diphenyl diisocyanate (MDI), dibutyltin dilaurate (DBTDL), and Cu^0 wire ($\geq 99\%$) were used as received from Sigma-Aldrich, USA. Polyoxytetramethylene glycol of molecular weight 1000 (PTMO; Merck, Germany) was purified by heating at 105°C under vacuum for 3 h before use. Benzophenone (99%; ABCR GmbH, Germany), $\text{Cu}^{\text{I}}\text{Br}_2$ (99.999%; Sigma-Aldrich, USA) were used without further purification. Tris(2-pyridylmethyl)amine (TPMA) was prepared according to the published procedure [37]. Styrene (St; 99%; Sigma-Aldrich, USA) were passed through a column filled with basic alumina prior to use to remove any inhibitor. Tetraphenylethane-1,2-diol (TPED) was prepared from benzophenone and 2-propanol in the presence of acetic acid as reported in the literature [35]. Tetraphenylethane-urethane macroinitiator (TPE-PU-TPE) was synthesized from PTMG, MDI, and TPED according to the published procedure ($M_n = 7600$ g/mol) [35]. Acetic acid (99.5%), cyclohexane (99.9%), methanol (99.9%), acetone (99.5%) and 2-propanol (99%) were obtained from Chempur, Poland. Analytical grade *N,N*-dimethylformamide (DMF; Sigma-Aldrich, USA) and methyl ethyl ketone (MEK; Sigma-Aldrich, USA), were distilled and the middle portions were used after storing over type 4 Å molecular sieves.

2.2. Characterization techniques

Molecular weights and molecular weight distributions were determined by GPC (Polymer Standards Services (PSS) columns (guard, 10^4 , 10^3 , and 10^2 Å), with THF eluent at 25°C , flow rate 1.00 mL/min, and with a differential refractive index (RI) detector (Viscotek, T60A)). The apparent molecular weights and dispersity (M_w/M_n) were determined with a calibration based on PS standards using TRISEC software from Viscotec Corporation. ^1H and ^{13}C NMR spectra of the macroinitiator and copolymers were

recorded on a FT-NMR Bruker Avance 500^{II} spectrometer using DMSO as a solvent and tetramethylsilane (TMS) as an internal standard. Monomer conversion and theoretical number-average molecular weight ($M_{n,th}$) were determined by NMR based on the previous research [31, 35].

2.3. Synthesis of urethane-styrene copolymers through SARA ATRP

The synthesis of tri-block copolymers was conducted, in the presence of 250 ppm of copper catalyst (Figure 2).

TPE-PU-TPE (5.09 g, 0.67 mmol) was placed in a Schlenk flask, and the flask was sealed with a glass stopper. The flask was evacuated and backfilled with nitrogen 5 times. Then, 20 mL of nitrogen purged DMF, 20 mL of N₂ purged St (18.12 g, 174 mmol) were added to the flask placed in an oil bath. Subsequently, 0.67 mL of Cu^{II}Br₂/2TPMA stock solution (0.05 M in DMF) was injected into the reaction solution. Next, Cu⁰ wire (0.77, 1.69, 2.60 or 3.52 g) was immersed in the reaction solution. To initiate the polymerization reaction mixture was heated to 90 °C. Samples were withdrawn periodically to follow monomer conversion, using ¹H NMR. The polymerization was stopped after 46 h by opening the

flask and exposing the catalyst to air. The products were purified by precipitation against MeOH, washed with cyclohexane, collected and dried under vacuum. Then the M_n and M_w/M_n were determined by GPC measurements (with PS standard curve).

2.4. Synthesis of urethane-styrene copolymers through radical polymerization

TPE-PU-TPE (5.09 g, 0.67 mmol) was placed in a Schlenk flask, and the flask was sealed with a glass stopper. The flask was evacuated and backfilled with nitrogen 5 times. Then, 20 mL of nitrogen purged DMF, 20 mL of N₂ purged St (18.12 g, 174 mmol) were added to the flask placed in an oil bath. To initiate the polymerization reaction mixture was heated to 90 °C. Samples were withdrawn periodically to follow the monomer conversion and M_n by ¹H NMR, and to determine M_w/M_n by GPC measurements with PS standard curve.

3. Results and discussion

In this paper SARA ATRP polymerizations of styrene in the presence of TPE-PU-TPE are reported for the first time. Polymerizations were conducted utilizing copper wire as an in situ reducing agent. The results are summarized in Table 1.

Figure 2. Synthesis of the urethane-styrene copolymers from tetraphenylethane-urethane macroinitiator [35, 38]

Table 1. SARA ATRP of PSt-*b*-PU-*b*-PSt utilizing copper wire

Entry	S/V^a [cm ⁻¹]	k_p^{appb} [h ⁻¹]	Conv ^b [%]	$M_{n,theo}^c$ ($\cdot 10^{-3}$)	$M_{n,GPC}^d$ ($\cdot 10^{-3}$)	M_w/M_n^d
1	0.09	0.027	70	26.6	27.0	1.29
2	0.19	0.031	75	27.9	28.8	1.28
3	0.29	0.034	79	28.9	29.6	1.26
4	0.39	0.041	84	30.4	31.0	1.18
5	–	0.003	13	11.1	13.3	2.38

General reaction conditions: $T = 90^\circ\text{C}$; $V_{tot} = 40\text{ mL}$, time = 46 h, copper wire ($L = 11, 24, 37$, and 50 cm , $d = 1\text{ mm}$); [St]:[TPE-PU-TPE calculated per 2 Br]:[Cu^{II}Br₂/2TPMA] = 130:1:0.05 (except entry 5: [St]:[TPE-PU-TPE calculated per 2 Br] = 130:1); [TPE-PU-TPE]₀ = 16.7 mM; [St]₀ = 4.3 M.

^aRatio of surface area (S) of Cu⁰ to total volume of reaction mixture (V);

^bMonomer conversion and apparent propagation rate constant (k_p^{app}) were determined by ¹H NMR, through the comparison of the integration of one vinyl proton of the remaining styrene at 5.25 ppm with the integration of the region at 7.96 ppm, which contained proton of the DMF;

^c $M_{n,theo} = ([M]_0/[I]_0) \cdot \text{conversion} \cdot M_{monomer} + M_{macroinitiator}$;

^d $M_{n,GPC}$ and MWD were determined by GPC with PS standards.

The effect of initiation system on the tri-block copolymer formation was evaluated by comparing radical polymerization and SARA ATRP systems (Table 1, entries 1–4 vs. 5, Figure 3a, 3b vs. Figure 4a, 4b). It was observed that the conventional radical polymerization of styrene was not controlled (Figure 3a, 3b), with broad polydispersity, MWD = 2.38 (Table 1, entry 5). In contrast, in the polymerizations conducted with TPE-PU-TPE/Cu^{II}Br₂/2TPMA/Cu⁰/St system, monomer conversion reached 70–84% and evolution of experimental MW with conversion followed the theoretical prediction (Figure 4a, 4b). In this case, contributions of side reactions are lower,

because SARA ATRP initiating system lower the concentration of primary radicals in the initiating step as in the case of normal ATRP. Briefly, a polymerization with TPE-PU-TPE/Cu^{II}Br₂/2TPMA/Cu⁰/St system were 9–14 times faster (compare k_p^{app} ; Table 1, entries 1–4 vs. 5) than with TPE-PU-TPE/St system.

3.1. Influence of the surface area of Cu to volume of reaction mixture ratio (S/V)

Since Cu⁰ in the form of a wire (Table 1, entries 1–4) acts as a supplemental, rather than the major activator of alkyl halides [17], four experiments were conducted with varying amounts of Cu⁰ surface area to solution volume ratio (S/V), from 0.09, 0.19, 0.29, to 0.39 cm⁻¹ (Figure 4a, 4b, 5a–5d, and 6). Figure 4 illustrates the polymerization kinetics and molecular weight evolution with conversion. In this case, as the surface area of Cu⁰ was decreased (S/V from 0.39 to 0.09 cm⁻¹), the rate of polymerization declined, k_p^{app} from 0.041 to 0.027 h⁻¹. These results suggest the involvement of Cu⁰ in the rate-determining step of the reaction, see Equation (1):

$$R_a = k_p^{app} \left(\frac{S}{V} \right) \quad (1)$$

where R_a is defined as an activation rate of macroinitiator [13]. Moreover, molecular weights increased linearly with conversion (Figure 4b), and were almost identical to theoretical ones. This result comes from maintaining a constant number of chains throughout the polymerization, which requires sufficiently fast initiation (all chains are propagated before the reaction is stopped) and an absence of chain transfer

Figure 3. Polymerization of St. (a) First-order kinetic plot, and (b) M_n and M_w/M_n versus monomer conversion. Reaction conditions: [St]:[TPE-PU-TPE calculated per 2 Br] = 130:1; [TPE-PU-TPE]₀ = 16.7 mM; [St]₀ = 4.3 M, $T = 90^\circ\text{C}$; $V_{tot} = 40\text{ mL}$.

Figure 4. SARA ATRP of St as a function of the ratio of surface area of Cu0 to total volume of reaction solution ($S/V = 0.09$, 0.19, 0.29, and 0.39 cm^{-1}). (a) First-order kinetic plot of monomer conversion versus time, and (b) M_n and M_w/M_n versus monomer conversion. Reaction conditions: $[\text{St}]:[\text{TPE-PU-TPE}]$ calculated per 2 Br $^-$: $[\text{Cu}^{\text{II}}\text{Br}_2/2\text{TPMA}] = 130:1:0.05$; $[\text{TPE-PU-TPE}]_0 = 16.7 \text{ mM}$; $[\text{St}]_0 = 4.3 \text{ M}$; $T = 90^\circ\text{C}$; $V_{\text{tot}} = 40 \text{ mL}$.

Figure 5. GPC traces during the SARA ATRP of St as a function of the ratio of surface area of Cu(0) reducing agent to total volume of reaction mixture ((a) $S/V = 0.9 \text{ cm}^{-1}$, (b) $S/V = 0.19 \text{ cm}^{-1}$, (c) $S/V = 0.29 \text{ cm}^{-1}$ and (d) $S/V = 0.39 \text{ cm}^{-1}$)

reactions (which increases the total number of chains) [39].

Furthermore, molecular weight distributions were independent of copper surface area and remained

low, with MWD = 1.18 at 84% of monomer conversion ($S/V = 0.39 \text{ cm}^{-1}$) (Figure 5d).

Importantly, because the reaction rate was dependent on the Cu^0 surface area to reaction volume ratio

Figure 6. Relationship between the apparent propagation rate constant (k_p^{app}) versus the square root of the surface area of Cu⁰ to total volume of reaction solution ($S/V = 0.09, 0.19, 0.29$, and 0.39 cm^{-1}). Reaction conditions: $[\text{St}]:[\text{TPE-PU-TPE calculated per 2 Br}]:[\text{Cu}^{\text{II}}\text{Br}_2/2\text{TPMA}] = 130:1:0.05$; $[\text{TPE-PU-TPE}]_0 = 16.7 \text{ mM}$; $[\text{St}]_0 = 4.3 \text{ M}$, $T = 90^\circ\text{C}$; $V_{\text{tot}} = 40 \text{ mL}$.

(S/V) and not on the total amount of copper used, it also seemed feasible to increase this rate by either increasing the surface area of metallic copper or decreasing total reaction volume [30]. As expected

a linear relationship between the k_p^{app} and the square root of (S/V) was observed [40] (Figure 6), due to the surface uniformity and monodispersity of Cu⁰ wire. It was demonstrated that the rate of polymerization (associated with k_p^{app}), scales appropriately with the approximate surface area of Cu⁰ utilized.

3.2. Chemical structure of the tri-block copolymers

The chemical structure of the synthesized PSt-*b*-PU-*b*-PSt tri-block copolymer (Table 1, entry 4) was confirmed by ¹H NMR and ¹³C NMR spectroscopy (Figure 7 and 8).

All the peaks corresponding to PU and PSt blocks are present in the ¹H and ¹³C NMR, which is a clear evidence for the formation of tri-block copolymer (Table 1, entry 4). In the ¹H NMR spectrum of copolymer (Figure 7), the CH protons of PSt (α) appear at 1.70–1.95 ppm and CH₂ protons of PSt (β) appear at 1.30–1.42 ppm. The phenyl protons of PSt generally appear at 6.20–6.80 ppm (z) and at 6.80–7.30 ppm (z' , z''), to some extent merged with the peak of phenyl protons of MDI. In the ¹³C NMR spectrum of

Figure 7. ¹H NMR spectrum of PSt-*b*-PU-*b*-PSt copolymers (Table 1, entry 4); $M_n = 31\,000$, $D = 1.18$) after purification (in DMSO)

Figure 8. ^{13}C NMR spectrum of PSt-*b*-PU-*b*-PSt copolymers (Table 1, entry 4); $M_n = 31\,000$, $D = 1.18$) after purification (in DMSO)

the urethane-styrene copolymer (Figure 8), the CH carbon atoms of PSt (α) appear at 29.01 ppm and CH_2 protons of PSt (β) appear at 35.89 ppm. The phenyl protons of PSt (30–33) appear at 125.54–135.56 ppm, to some extent merged with the peak of phenyl protons of MDI.

The formation of a tri-block structure can be assumed based on the use of a symmetrical macroinitiator, but obtainment of precisely symmetrical tri-block copolymers cannot be supported by the NMR data.

4. Conclusions

Tetraphenylethane-urethane macroinitiator (TPE-PU-TPE) has been used to synthesize polystyrene-*b*-polyurethane-*b*-polystyrene (PSt-*b*-PU-*b*-PSt) tri-block copolymers through supplemental activator and reducing agent atom transfer radical polymerization (SARA ATRP). The influence of surface area of Cu^0 acting as a supplemental activator of alkyl halides and a reducing agent for excess Cu^{II} on the

polymerization was examined. Excess of reducing agent slightly accelerates ATRP but does not interfere with the controlled growth. The DP of the resulting copolymers increased linearly with monomer conversion and semilogarithmic kinetic plots were linear, which confirmed the living nature of the SARA ATRP of styrene. The results from ^1H and ^{13}C NMR spectral studies support the formation of PSt-*b*-PU-*b*-PSt tri-block copolymers. Therefore SARA ATRP – method without pre-disproportionation of Cu^{I} species provide a powerful tool for the synthesis of a broad range of copolymers with controlled chain length and narrow molecular weight distributions.

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