



Copolymerization of Styrene and [Poly(ethylene glycol) methyl ether] Methacrylate using Reverse Atom Transfer Radical Polymerization

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Abstract: Well-defined amphiphilic copolymers of styrene and poly(ethylene glycol) methyl ether methacrylate (PEGMA) were successfully synthesized using reverse atom transfer radical polymerization (RATRP). The initial feed ratio of the macromonomer, PEGMA has a significant effect on the copolymer yield. Copolymer yield decreased with increasing the monomer feed ratio of PEGMA, but number average molecular weight followed the opposite trend. The resultant copolymers were characterized by nuclear magnetic resonance (NMR) spectroscopy to confirm their structures and comonomer compositions. The macromonomer content in the copolymer has a significant effect on the thermal and mechanical properties.

Keywords: Styrene; Copolymers; Macromonomer; RATRP; Mechanical properties

1. Introduction

Atom transfer radical polymerization (ATRP) is one of the most promising approaches for controlled radical polymerization.^[1] ATRP can be used in two different initiating systems: (a) an alkyl halide and transition- metal compound in its lower oxidation state of CuBr complexed by two molecules of ligand for example 4,4'-di(alkyl)-2,2'-bipyridine or one molecule of N,N,N',N''-pentamethyldiethylenetriamine^[2-4] (b) a conventional radical initiator such as azobis(isobutyronitrile) (AIBN) with the transition-metal compound in its higher oxidation state of CuBr₂ complexed by an appropriate ligand.^[5] The latter approach has been named reverse atom transfer radical polymerization (RATRP) and was successfully used for copper-based heterogeneous and homogeneous systems in solution and in emulsion as well as for iron complexes.^[5,6] These systems successfully used to prepare polymers with predetermined molecular weights, low polydispersity (PDI), and precise end functionalities as well as a variety of copolymers with controlled topologies and compositions.^[2,3]

Styrene is one of the most common monomer among the monomers used in polymerization.^[7] Polystyrene (PSt) is not only important in academic research but also in industrial research

because it may exhibit excellent properties such as good heat and chemical resistance, high decomposition temperature, high optical transparency and low birefringence.^[8] The PSt is normally brittle and carried high glass transition temperature (T_g).

The properties as well as T_g value can be controlled using suitable co-monomers composition. The copolymers of styrene (St) can be obtained from different of polymerization system such as coordination,^[9] anionic^[10] and controlled radical polymerization (CRP).^[11] The presence of soft segment for example ethylene, α -olefines and methacrylate derivatives in PSt chain shows excellent properties with controlled T_g values.^[12-16] CRP is the most convenient way to copolymerize St with polar monomer such as methacrylate derivatives because of catalytic poisoning or side reaction occurred in coordination and anionic polymerization.

Acrylic-type macromonomers combine the productivity of radical polymerization with high molecular weight polymers with easily tunable degradation time,^[17] charge density,^[18] lower critical solution temperature (LCST),^[19] etc. Poly ethylene glycol (PEG)-based polymers are of interest for a broad range of applications such as biocompatible coatings for magnetic resonance tomography contrast agents,^[20] drug delivery systems,^[21] surfactants,^[22] and for the synthesis of bioconjugates.^[23] Polymers with short PEG side chains

are applied as dental soft lining materials^[24] and as polymeric gel electrolytes in lithium batteries.^[25]

Copolymerization of styrene and macromonomer is particularly attractive because of well-defined graft properties efficiently impart onto the polymer chain. Furthermore, these macromolecules may exhibit stimuli-responsive properties, which are typically not attainable with linear polymer. For instance, these graft polymers generally display a LCST in pure water or in physiological medium.^[26] Nonlinear poly(ethylene glycol) methyl ether methacrylate (PEGMA) analogues should appear as ideal structures, which combine both the properties of PEGMA and St in a single macromolecule. Therefore, we are interested to introduce a well-defined PEGMA branch chain into the PSt backbone for tuning the thermal and mechanical properties. In the present paper, we report the copolymerization of St with a macromonomer of PEGMA using RATRP system which is one of the most convenient polymerization method for copolymerization of macromonomers.^[27]

2. Experimental Section

2.1. General considerations

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk-line techniques. All solvents were distilled from sodium/benzophenone or CaH₂. St (Sigma–Aldrich) was dried over CaH₂ and then freshly distilled under vacuum prior to use. PEGMA (*M_n* 300 g mol⁻¹, Sigma–Aldrich) was activated prior to use by passing through a column with alternating layers of basic aluminum oxide (activated) to remove inhibitor. CuBr₂, bipyridine, and 2,2'-azobisisobutyronitrile (AIBN) were obtained from Sigma–Aldrich and used as received.

2.2. Analytical procedures

The molecular weight and polydispersity of the polymers were determined by gel-permeation chromatography (GPC) with TOSOH HLC-8320 liquid Chromatograph equipped with an RI detector, using dry THF as the mobile phase. The ¹H and ¹³C NMR spectra of the polymers were measured at room temperature on a Bruker 500 MHz spectrometer (Bruker, Germany) operated in pulse Fourier-transform mode. The sample solutions for the ¹H and ¹³C NMR measurements were prepared in CDCl₃ with concentrations of up to 5 wt%. The pulse angle was 45°, and approximately 500 scans were accumulated for the ¹³C NMR spectra with a pulse-repetition delay of 5.0 s. The peak of residual CHCl₃ in CDCl₃ (¹H NMR: 7.25 ppm; ¹³C NMR: 77.13 ppm) was used as an internal reference. Differential scanning calorimetry (DSC) was performed on an SII EXSTER 600 (Seiko Instruments Inc., Japan) system under a nitrogen atmosphere. Differences in the thermal history of the polymers were eliminated by first heating the specimen to 400 K, cooling it to 200 K, and then recording the second DSC scan (all heating rates: 10 K/min). Thermogravimetric analyses (TGA) were carried out using a TG/DTA 6300 analyzer (Seiko Instruments Inc., Japan) under a flow of nitrogen (constant heating rate: 10 °C/min; 25 → 450 °C). UV-Vis spectra were recorded on a UV-2600 (Shimadzu Corporation, Japan) system under ambient conditions.

2.3. Homo and copolymerization of St and PEGMA

The homopolymerization of St or copolymerization with PEGMA was synthesized as follows: St (5 mmol) [added PEGMA (1 mmol) for copolymerization], were added in 2 mL of toluene into a 10 mL Schlenk equipped with a magnetic bar with five freeze-pump thaw cycles to remove the remaining oxygen. CuBr₂ (11.6 mg, 0.118 mmol) and bpy (36.8 mg, 0.236 mmol) were added quickly to the flask, and one more freeze-pump-thaw cycle was carried out. AIBN (13 mg, 0.059 mmol) dissolved in 1 mL of toluene was then added to the reaction Schlenk. The solution was then degassed with nitrogen, and subsequently placed in a preheated oil bath at 70°C to carry out RATRP polymerization. The polymerization reactions were terminated by adding 50 mL of methanol. The resulting precipitated polymers were collected by filtration, adequately washed with methanol, and dried under reduced pressure.

2.4. Preparation of copolymer film by the solution casting

The copolymers (approximately 300 mg) were dissolved in chloroform (3 mL) at room temperature and filtered through a 0.20 μm polytetrafluoroethylene (PTFE) membrane. The filtered solution was placed on a PTFE petri dish and allowed to stand for 3 days at ambient temperature and pressure. After almost all the solvent had evaporated, the film was dried for 3 h under reduced pressure.

3. Results and Discussion

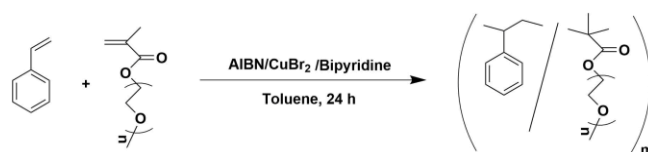
3.1. Homopolymerization of St

Homopolymerization of St was conducted by reverse atom transfer radical polymerization (RATRP) using different initiator /catalyst feed ratio at 70 °C in toluene. The results are summarized in Table 1. The highest activity of 95% was achieved in 6h at the ratio of AIBN/CuBr₂/bpy (1/2/4). This condition was not only provided the highest activity but also gave the polymer with the highest molecular weight with very low PDI (≈ 1.1) than the other initiator-catalyst feed ratio (Table 1, run 3).

3.2. Copolymerization St and PEGMA

Considering the best condition for St Polymerization, copolymerization of St with PEGMA was also carried out using the same initiator/catalyst feed ratio. Such polymer showed branched structure composed of a carbon–carbon backbone of St and multiple oligo(ethylene glycol) side-chains of PEGMA (Scheme 1).

Copolymerization of St/PEGMA showed good conversion at all monomer feed ratios but needed longer polymerization time than the homopolymerization of St. As a result, lower conversion was observed in the copolymerization than the homopolymerization

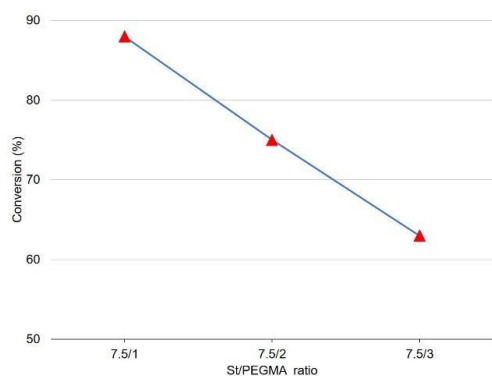
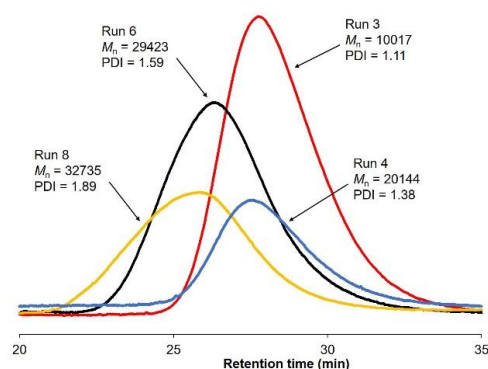


Scheme 1. Copolymerization of St and PEGMA.

Table 1. Copolymerization of St and PEGMA macromonomer.^a

Run	Mono. Ratio (mmol/mmol)	[AIBN] ₀ /[CuBr ₂] ₀ /[Bpy] ₀	Time (h)	Conv. (%)	M _n ^b	PDI	St cont. ^c	T _g ^d (K)
1	St (5)	1/0/0	6	97	9118	2.36	100	-
2	St (5)	1/1/2	6	93	7993	2.13	100	-
3	St (5)	1/2/4	6	95	10017	1.11	100	371
4	St/PEGMA (10.0/1)	1/2/4	24	91	20144	1.38	91	297
5	St/PEGMA (7.5/1)	1/2/4	24	88	23169	1.45	87	275
6	St/PEGMA (5.0/1)	1/2/4	24	83	27534	1.59	83	262
7	St/PEGMA (7.5/2)	1/2/4	24	75	29423	1.64	77	255
8	St/PEGMA (7.5/3)	1/2/4	24	63	32735	1.89	70	231

^aPolymerization condition: Temperature = 70 °C. ^bDetermined by size exclusion chromatography (GPC). ^cThe content of St in the St/PEGMA copolymer determining by ¹H NMR spectrum. ^dDetermined by DSC.

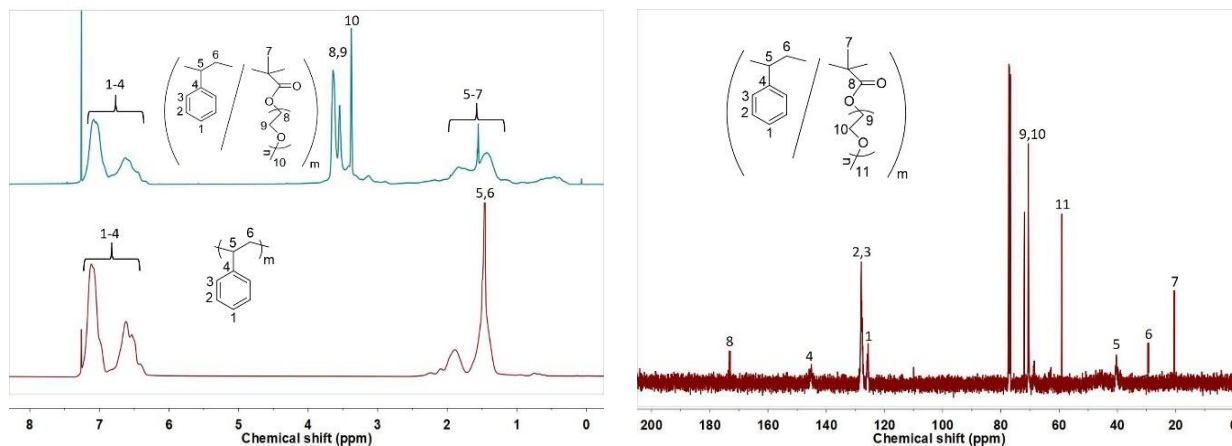
**Fig. 1.** Plot of Conversion against monomer feed ratio**Fig. 2.** GPC traces of St/PEGMA copolymers

of St. The co-monomer significantly affects the catalytic activity and the copolymerization yield decreased with increasing the PEGMA ratio from 1 to 3 mmol in monomer feed (Fig. 1). The highest conversion of 91 % was obtained with the lowest co-monomer feed ratio of 10.0/1 [St/PEGMA] (Table 1, Run 4).

The molecular weight of St/PEGMA copolymer was measured by GPC. The increase of PEGMA concentration from 1 to 3 mmol in monomer feed caused the increase in the molecular weights of the produced polymers (Fig. 2) and the PDI was also increased from 1.4 to 1.8 (Table 1, Run 4-8). The highest M_n of 32735 g/mol was

observed with highest PEGMA ratio with 3 mmol. Unimodal distribution (PDI < 2) indicates that the successful copolymerization.

The incorporation of St in the produced copolymers was investigated by ¹H NMR in CDCl₃. A typical ¹H NMR spectrum of the PSt and St/PEGMA copolymer (Run 7) is illustrated in Fig. 3. The signals attributed to the aromatic protons of the St Units (H¹⁻⁴) are observed in the range of 6.5–7.1 ppm. The signals assignable to the aliphatic protons of the St and PEGMA units (H^{5,6} and H⁷) are observed in the range of 1.2–2.1 ppm. Particularly, the signal of the methylene (-OCH₂) and methyl (-OCH₃) proton of the PEGMA unit can

**Fig. 3.** ¹H NMR spectrum of St (Table 1, Run 3) and ¹H NMR spectrum and ¹³C NMR spectra of St/PEGMA copolymer obtained by Run 7 (CDCl₃, 25 °C, 500 MHz).

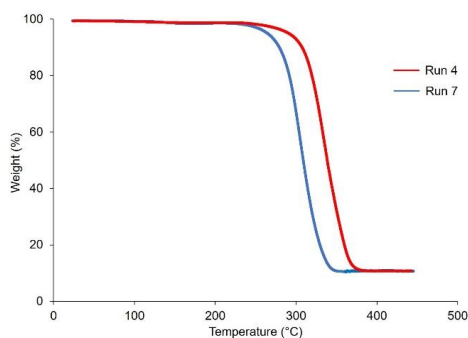


Fig. 4. TGA traces of St/PEGMA copolymer.

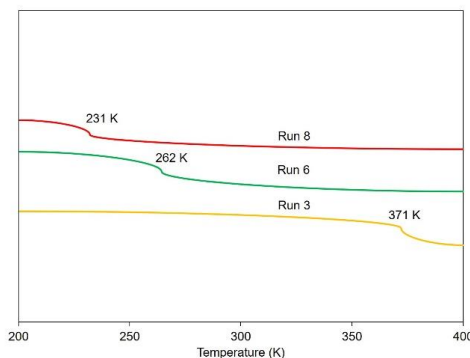


Fig. 5. DSC traces of St/PEGMA copolymer.

be observed at 3.6-3.75 and 3.4 ppm. The incorporation of St decreased with decreasing St Concentration in the monomer feed ratio (Table 1, Run 4-8). The highest St Content in the St/PEGMA copolymer was achieved to be 91% at the feed ratio of 10:1 (St/PEGMA) (Table 1, Run 4).

A typical ^{13}C NMR spectrum of the copolymer (Run 7) is shown in Fig. 3. The signals of each chemical shift region were assigned as follows: 127.9 ppm for C^1 , 128.5 and 128.9 ppm for $\text{C}^{2,3}$, 143.7 for C^4 , 40.5 and 30.3 ppm for C^5 and C^6 of the St segment, 20.1 ppm for C^7 , 177.7 ppm for C^8 , 71 and 71.8 ppm for $\text{C}^{9,10}$, and 59.3 ppm for C^{11} of the PEGMA unit. A clear observation of the phenyl-carbons of the St Units also indicates the presence of the St Units in the St/PEGMA copolymer and confirms the random distribution of PEGMA unit in the obtained St/PEGMA copolymer.

3.3. Thermal properties

The thermal properties of the St/PEGMA copolymers were investigated by thermogravimetry-differential thermal analysis (TG-DTA) and differential scanning calorimetry (DSC). The degradation temperature with 5% weight loss of PSt was obtained at 330 °C. The degradation temperature was decreased with increasing the branching density of PEGMA. The degradation temperature (5% weight loss) of St/PEGMA copolymer with 91 mol% St was obtained at 321 °C that was very close to the PSt but the values was decreased to 293 °C for 70 mol% St (Fig. 4). The corresponding DTA curves showed endothermic peak and suggesting the thermal stability of the copolymer.

The T_g value of the copolymer of St/PEGMA was varied according to the PEGMA content. The PSt showed higher T_g value as high as 371 K. The T_g value decreased from 321 to 297 K with only 7 mol % of PEGMA content. According to the PEGMA content, the T_g value gradually decreased with increasing the PEGMA content and the value observed from 297 to 231 K (Table 2, Run 3-8; Fig. 5).

3.4. Optical property of the St/PEGMA copolymer

PSt is rather brittle because it has poor impact strength due to the stiffness of the polymer backbone and lack of crystallinity.^[28] Increasing the branching density using PEGMA decreased the brittleness and increased the flexibility in physical appearance of the copolymer film because copolymer with the highest PEGMA content (Table 1, Run 8) only showed gummy product. The light transmittance was measured for the St/PEGMA copolymer thin film

with the thickness about 120 μm . The copolymer showed the transmittance around 85% (Table 1, Run 6) in the visible light region (400–800 nm) which is close to the PSt film.^[29]

4. Conclusions

Well-defined amphiphilic St/PEGMA copolymers were obtained by adopting the RATRP method. The highest conversion was observed at the lowest feed ratio of macromonomer PEGMA. On the other hand, the M_n was increased and PDI was broadening with the highest PEGMA ratio in monomer feed. Thermal and mechanical properties were controlled by the PEGMA content. The copolymer with high content of PEGMA showed lowest T_g value with high flexibility.

Acknowledgements

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Conflicts of Interest

The authors declare no conflict of interest

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