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Synthesis and Characterization of UV Crosslinkable and Highly Sulfonated Block Copolymer by Living Radical Polymerization

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UV crosslinkable sulfonated block copolymers of neopentyl p-*styrene sulfonate (NSS) and 2-cinnamoylethyl acrylate (CEA) were synthesized by living radical polymerization. For this, the block copolymers of 2-(trimethylsilyl)ethyl acrylate (TMSEA) and NSS were first synthesized by sequential CuBr catalyzed living radical polymerization with 2-bromopropionate (EBP) initiator and* N,N,N′,N′-*pentamethylethyleneamine (PMDETA) ligand. Obtained well defined block copolymers (polydispersity <1.21) were then hydrolyzed with an acid to give the block copolymer of 2-hydroxylethyl acrylate (HEA) and NSS. Cinnamoyl chloride as a crosslinking moiety reacted with the hydrolyzed block copolymers to give final UV crosslinkable sulfonated block copolymers. Theses block copolymers were successfully crosslinked under UV irradiation and generated sulfonic acid groups by thermolysis of the PNSS.*

Introduction

Well defined polymer electrolyte membrane is important to increase the efficiency of both proton exchange membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFC), which usually requires high proton conductivity, low fuel crossover, and high mechanical and chemical stabilities [1]. Among several polymer electrolyte membranes, sulfonated styrene based block copolymers such as sulfonated poly (styrene-(ethylene-co-butylene)-styrene) and poly(styrene-isobutylene-styrene) are especially interesting, because such hard-soft block copolymer ionomers can be used to control self-assembled morphology, in which one domain of micron or nanometer size will be ionic and the other insulating [2,3]. Synthesis of these sulfonated block copolymers are usually carried out by post sulfonation of the polystyrene block segment using sulfonating agents such as acetyl sulfate or sulfur trioxide [4]. However, since introduction of sulfonic acid groups on the styrene based block copolymer is not easy to control, especially at high sulfonation levels, due to extremely different polarity between block segments. Thus, synthesis by direct block copolymerization of sulfonated styrene is a more easily achievable method to prepare styrene block

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copolymers with high sulfonation levels. I recently reported synthesis of well defined sulfonated poly(styrene-*block*-*n*-butyl acrylate) (PDI < 1.11) by block copolymerization of neopentyl styrene sulfonate (NSS) using a poly(*n*-butyl acrylate) macroinitiator in a CuBr catalyzed living radical polymerization system followed by thermolysis to give fully sulfonated polystyrene block segment [5]. However, the high number of sulfonic acid groups in the block copolymer led to dissolution of the solid in water due to the formation of micelles. To overcome this problem, a UV crosslinkable segment, poly(2-cinnamoylethyl acrylate) (PCEA), was introduced into the sulfonated polystyrene block copolymer. In this study, synthetic feasibility of this CEA-NSS block copolymer and the possibility for electrolyte membrane with high sulfonation level in crosslinked matrix.

Experimental

Materials

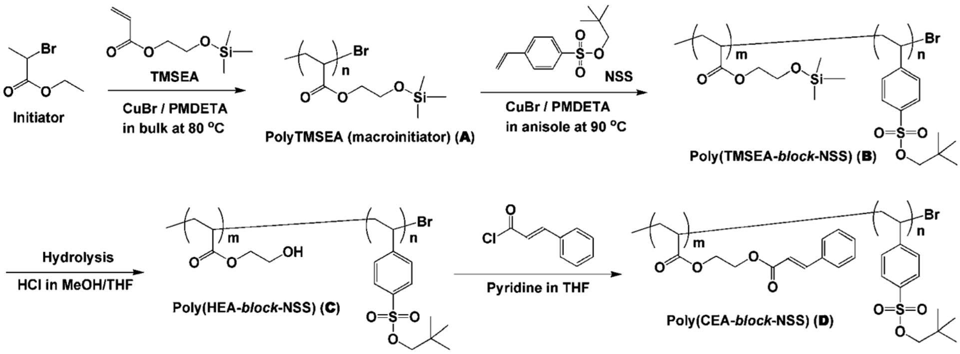
2-(trimethylsiloxy)ethyl acrylate (TMSEA) was prepared according to the literature [6]. Neopentyl styrene sulfonate (NSS) was prepared according to the literature [5]. CuBr (Aldrich, 99.999%) was used as received. Ethyl 2-bromopropionate (EBP, Aldrich, 99%) was distilled from calcium hydride before use. *N*,*N*,*N'*,*N'*-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%) was distilled from calcium hydride before use. Cinnamoyl chloride (Aldrich, 98%) was used as received. Anisole and THF (solvent) was purified by distillation from calcium hydride before use.

General Synthetic Procedure for CEA-NSS Block Copolymers

A polymerization of TMSEA was first carried out in the CuBr catalytic system with EBP initiator and PMDETA as a ligand (TMSEA/EBP/CuBr/PMDETA = 50/1/1/2) in bulk at 80°C under argon according to the literature [6]. Obtained well defined PTMSEA ($M_n = 10{,}200$; $MWD = 1.23$) was used as a macroinitiator for further block copolymerization of NSS. A typical polymerization procedure with NSS/PTMSEA macroinitiator/CuBr/PMDETA (40/1/1/2) in anisole at 90°C under argon was carried out according to the literature [5]. Obtained TMSEA-NSS block copolymer ($M_n = 19{,}100$; $MWD = 1.21$) was reacted with a small amount of HCl (~1 vol.%) in a methanol/THF mixture. Obtained 2-hydroxylethyl acrylate (HEA)-NSS block copolymers was reacted with excess amount of cinnamoyl chloride (~5 equiv. to HEA unit) in the presence of pyridine in THF. Final product was dissolved in small amount of THF and poured into methanol. Final product was dissolved in THF and precipitate into methanol, which was then filtered and dried overnight under vacuum at room temperature.

Measurements

The number average molecular weight (M_n) and molecular weight distributions (M_w/M_n) of the polymers were measured by Waters 150CV plus SEC system equipped with a differential refractive index detector and a M486 UV detector (254 nm detection wavelength) using THF as the mobile phase at 45°C and a flow rate of 1 mL/min. The samples were separated through four 5 µm PL Gel columns (Polymer Laboratories). ^{1}H spectra were recorded in $CDCl_3$ at 25°C on a Bruker AMX 300 (^{1}H: 300 MHz) or Bruker AM-400 (^{1}H: 400 MHz) spectrometer.



Scheme 1. Synthesis of crosslinkable sulfonated CEA-NSS block copolymers.

Result and Discussion

Crosslinkable sulfonated CEA-NSS block copolymers were synthesized as shown in Scheme 1. Thus, poly[2-(trimethylsiloxy)ethyl acrylate] (PTMSEA) (**A**) was first synthesized by CuBr catalyzed living radical polymerization with 2-bromopropionate as the initiator (EBP), *N*,*N*,*N*′,*N*′-pentamethyldiethylenetriamine (PMDETA) in bulk at 80°C ($M_n = 10{,}200$, $MWD < 1.23$) [6]. The obtained poly(TMSEA) was then used as a macroinitiator to polymerize NSS in the presence of CuBr with PMDETA in bulk at 90°C to give a well defined TMSEA-NSS block copolymer (**B**). These block copolymers were then hydrolyzed with a small amount of HCl in a methanol/THF mixture to give 2-hydroxylethyl acrylate (HEA)-NSS block copolymers (**C**), followed by reaction with cinnamoyl chloride in the presence of pyridine in THF to give CEA-NSS block copolymers (**D**) (Table 1).

Figure 1 shows GPC curves of obtained PTMSEA macroinitator, TMSEA-NSS block copolymer and final CEA-NSS block copolymer. The curve trace of TMSEA-NSS block copolymer was clearly shifted to high molecular weights in comparison to that of PTMSEA macroinitiator, indicating the successful formations of the block copolymers (Figs. 1A and 1B). However, the curve of CEA-NSS block copolymer was not much changed after introduction of cinnamoyl group instead of TMS group (Fig. 1C).

PTMSEA macroinitator and a series of the block copolymers were then characterized by ^{1}H NMR analyses (Fig. 2). Figure 2B shows the absorption peaks

Table 1. Molecular weight and molecular weight distribution of obtained block copolymers[a]

Polymer structure	m/n[b]	M_n[c] (SEC)	M_n (^{1}H NMR)	M_w/M_n (SEC)
$(\mathrm{TMSEA})_m$-*block*-$(\mathrm{NSS})_n$ (**B**)	54/15	15,200	14,000	1.18
	54/24	19,100	16,300	1.21
$(\mathrm{CEA})_m$-*block*-$(\mathrm{NSS})_n$ (**D**)	54/15	14,000	17,100	1.31
	54/24	20,600	19,400	1.22

[a] PTMSEA was used as a macrointiator ($M_n = 10{,}200$, $M_w/M_n = 1.23$) for polymerization of NSS: NSS/PTMSEA(MI)/CuBr/PMDETA (40/1/1/2) in anisole at 90°C.

[b] Monomer ratio was calculated from ^{1}H NMR spectra.

[c] Molecular weight based on PMMA standard in SEC analysis.

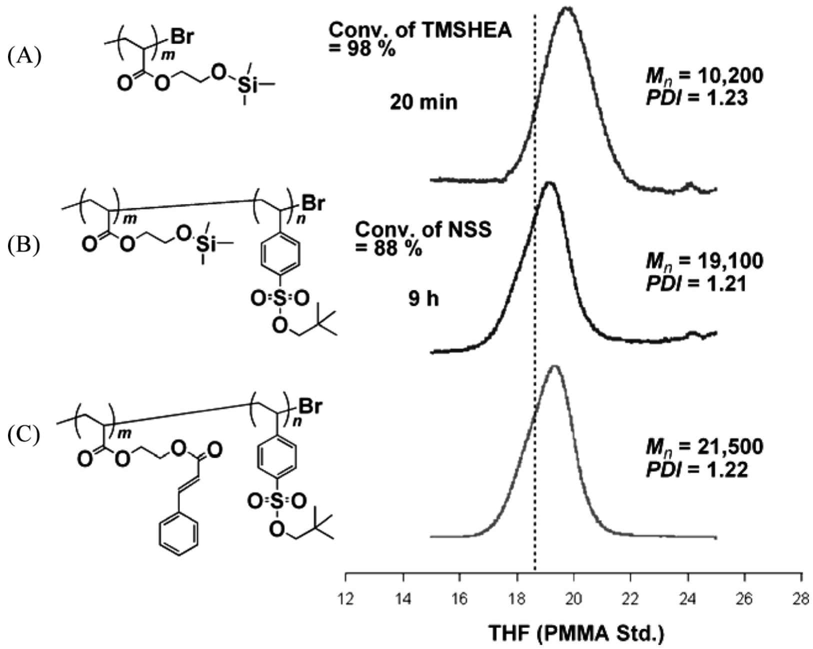


Figure 1. SEC curves of (A) PTMSEA macroinitiator, (B) TMSEA-NSS block copolymer, and (C) CEA-NSS block copolymer.

assigned to PNSS in conjunction with those assigned to PTMSEA (Fig. 2A), which indicated that NSS was quantitatively polymerized from the PTMSEA macrointiator to give well defined TMSEA-NSS block copolymer. The molar TMSEA/NSS ratio was determined to be 54/24, based on the integration of the methyl peaks of TMS group in PTMSEA (e) and the methyl peaks of neopently groups in PNSS (k). Figure 2C shows ^{1}H NMR spectrum of the hydrolyzed HEA-NSS block copolymer in CD_3OD after acid treatment. Deprotection of TMS group from PTMSEA was confirmed by the disappearance of the methyl proton peaks (e) of TMS group. In Figure 2D, absorption peaks originated from cinnamoyl group was additionally appeared and the ethylene peaks (c and d) in PHEA was shifted, which indicated that CEA group was qualitatively introduced into HEA-NSS block copolymer to give CEA-NSS block copolymer.

The block copolymer was then made into thin films by spin coating followed by irradiation with UV at 250 nm to give a crosslinked sulfonated block copolymer. FT-IR analysis showed that the peak originated from the double bond (1637 and 1710 cm^{-1}) of cinnamoyl group quantitatively decreased with the irradiation time but it was not completely disappeared (Figue 3). Although crosslinking reaction was not perfect, obtained film was free standing and insoluble in any organic solvents.

This film state of the crosslinked NSS block copolymer was then acidified by thermolysis at 150°C. Figure 4 shows FT-IR spectra before and after thermolysis of the crosslinked NSS block copolymer. The peaks of the sulfonate ester groups in PNSS at 1360 and 1480 cm^{-1} were decreased after thermolysis. This result indicates that the sulfonic acid group was quantitatively introduced to the styrene block segment in the crosslinked polymers.

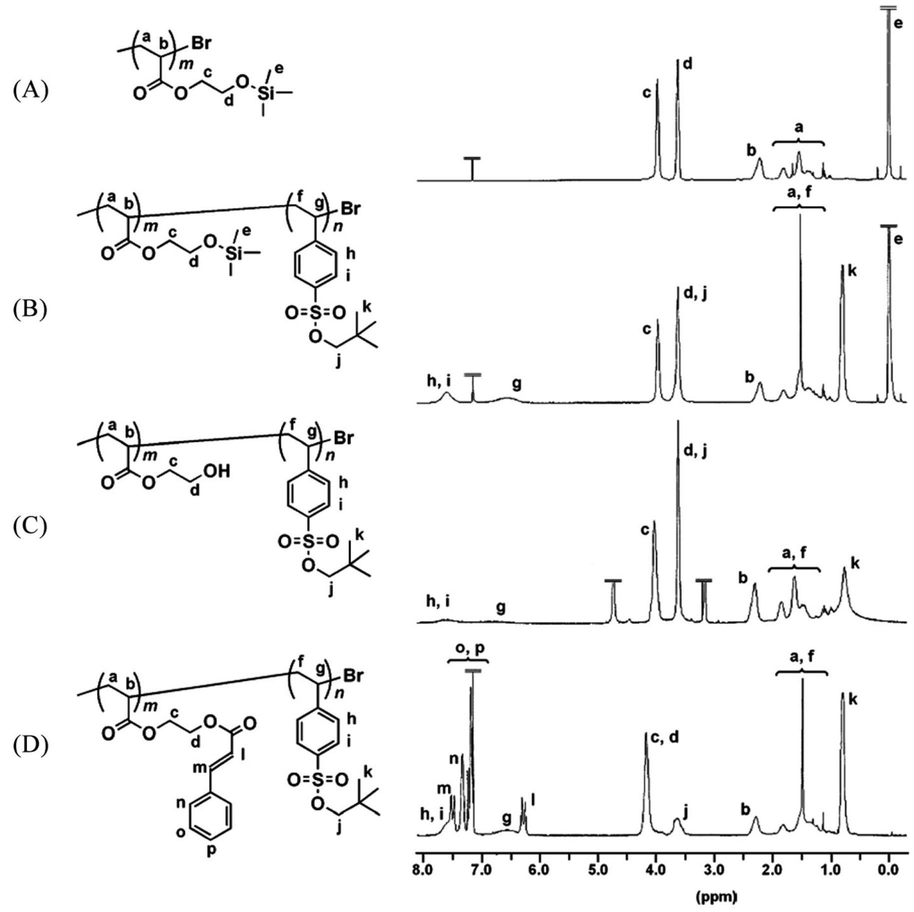


Figure 2. ^{1}H NMR spectra of (A) PTMSEA macroinitiator, (B) TMSEA-NSS block copolymer, (C) HEA-NSS block copolymer, and (D) CEA-NSS block copolymer. (A-B and D) were measured in $CDCl_3$ and (C) was measured in CD_3OD.

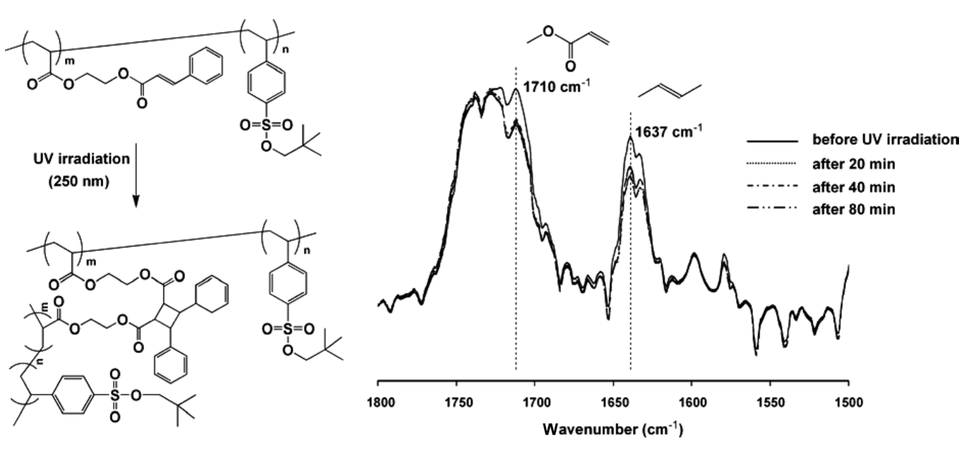


Figure 3. FT-IR spectra of crosslinked block copolymer after UV irradiation to CEA-NSS block copolymer thin film.

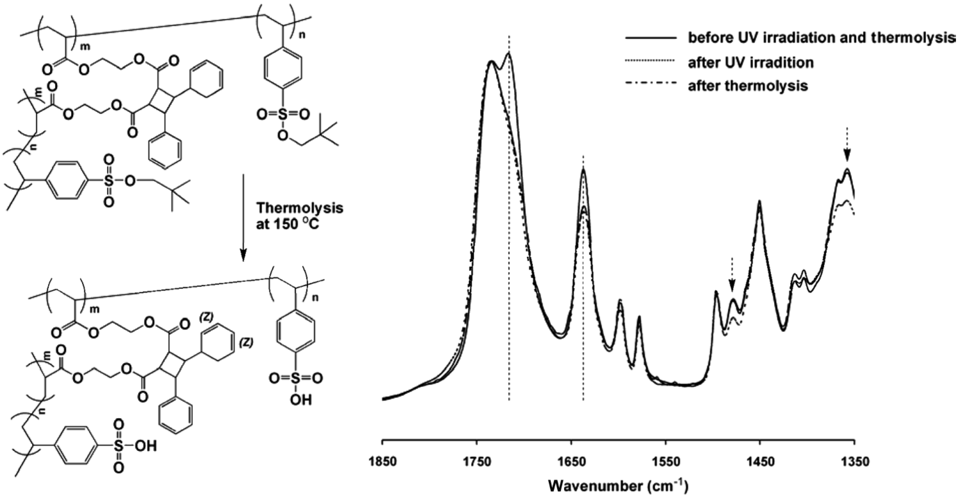


Figure 4. FT-IR spectra of crosslinked sulfonated block copolymer after UV irradiation to CEA-NSS block copolymer thin film followed by thermolysis at 150°C.

Conclusions

This study successfully demonstrated synthesis of UV crosslinkable sulfonated block copolymers by CuBr catalyzed living radical polymerization. Solid thin film state of the CEA-NSS block copolymers were successfully crosslinked by UV irradiation and generated sulfonic acid group in the polystyrene chain by simple heating process (thermolysis). Morphology, mechanical stability and electrochemical studies for PEMFC application will be discuss in forthcoming paper.

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References

[1] (a) Li, Q., He, R., Jensen, J. O., & Bjerrum, N. J. (2003). *Chem. Mater.*, *15*, 4896; (b) Hickner, M., Ghassemi, H., Kim, Y. S., Einsla, B. R., & McGrath, J. E. (2004). *Chem. Rev.*, *104*, 4587.

[2] (a) Weiss, R. A., Sen, A., Pottick, L. A., & Willis, C. L. (1991). *Polymer*, *32*, 2785; (b) Elabd, Y. A., Walker, C. W., & Beyer, F. (2004). *J. Mem. Sci.*, *231*, 181; (c) Kang, S. W., Choi, S. K., Choi, H.-M., Hwang, S. S., & Baek, K.-Y. (2009). *Macromol. Res.*, *7*, 455.

[3] (a) Eisenberg, A. & Kim, J.-S. (1998). *Introduction to Ionmers*, Wiley-Interscience: New York, 307–314; (b) Bates, F. S. & Fredrickson, G. H. (1990). *Ann. Rev. Phy. Chem.*, *41*, 525.

[4] Kucera, F. & Jancar, J. (1998). *Polymer Eng. Sci.*, *38*, 783.

[5] Baek, K.-Y. (2008). *J. Polym. Sci. Part A: Polym. Chem.*, *46*, 5991.

[6] Mühlebach, A., Gaynor, S. G., & Matyjaszewski, K. (1998). *Macromolecules*, *31*, 6046.