

Synthesis and Characterization of Poly(vinyl alcohol-*b*-styrene) via Atom Transfer Radical Polymerization and Saponification

Guang Hua Li and Chang Gi Cho*

Center for Advanced Functional Polymers, Department of Fiber & Polymer Engineering, Graduate School of Advanced Materials and Chemical Engineering, Hanyang University, 17 Haengdang-dong, Seongdong-gu, Seoul 133-791, Korea

Received Sept. 19, 2002; Revised Oct. 28, 2002

Abstract: Poly(vinyl alcohol-*b*-styrene) (poly(VA-*b*-St)) diblock copolymer containing high syndiotactic poly(vinyl alcohol) (PVA) was synthesized by the saponification of poly(vinyl pivalate-*b*-styrene) (poly(VPi-*b*-St)). For the block copolymer, poly(vinyl pivalate) (PVPi) with trichloromethyl end group was obtained via telomerization of vinyl pivalate with carbon tetrachloride as a telogen and 2,2-azobisisobutyronitrile (AIBN) as an initiator. Then resulting poly(vinyl pivalate) with trichloromethyl end group was used as an efficient macroinitiator for the synthesis of poly(VPi-*b*-St) using atom transfer radical polymerization (ATRP) in the presence of CuCl/2,2'-bipyridine at 130 °C. The poly(vinyl pivalate) macroinitiator, poly(VPi-*b*-St), poly(VA-*b*-St) were characterized by GPC, FT-IR and ¹H-NMR. And the analysis showed that integrity of the block copolymer was maintained during saponification reaction.

Keywords: radical telomerization, vinyl pivalate, atom transfer radical polymerization, styrene, block copolymer, poly(vinyl alcohol-*b*-styrene), poly(vinyl pivalate-*b*-styrene).

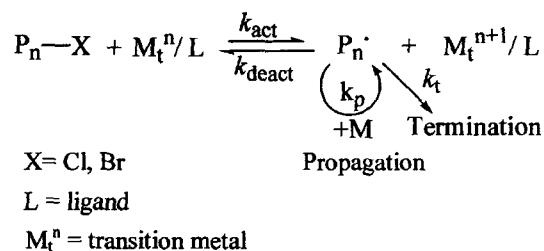
Introduction

The increasing importance and interest in block copolymers arises mainly from their unique properties in solution and in the solid state, which are a consequence of their molecular structure.¹ It was reported that poly(vinyl alcohol-*b*-styrene) (poly(VA-*b*-St)) with hydrophilic and hydrophobic, crystalline and non-crystalline blocks, shows the intriguing phenomenon of self-assembling of the amphiphilic copolymer and unique phase structure,²⁻⁷ and therefore which may be applied to coatings, adhesives, thin films, emulsion stabilization, pharmaceuticals, drug delivery, dispersion systems, and composite materials.^{2,3,5}

Poly(VA-*b*-St) diblock copolymer has been reported to be prepared by initiation of the polymerization of styrene and vinyl acetate followed by hydrolysis, using the ethanolamine-benzophenone charge-transfer complex³ or iniferter such as dithiocarbamate compounds⁸ under UV irradiation. Poly(VA-*b*-St-*b*-VA) triblock copolymer may be prepared by a binary system composed of polystyrene with *N,N*-dimethylaniline end groups and benzophenone or the polystyrene obtained from radical living polymerization of styrene with tetramethyltiuram disulfide as iniferter to initiate the poly-

merization of vinyl acetate under UV irradiation and followed by hydrolysis.^{2,9}

In recent years, atom transfer radical polymerization (ATRP) has attracted much attention.¹⁰⁻¹⁹ It is based on the combination of an organic or polymeric halides initiator with a metal/ligand catalytic systems, which reversibly activate halogenated chain ends (P_nX) during polymerization as shown in Scheme I.^{11,12,20,21} ATRP can be nicely applied to the synthesis of a block copolymer by sequential addition polymerizations of two monomers or by transformation reactions associated with other living processes. Matyjaszewski *et al.* reported the synthesis of poly(vinyl acetate-*b*-styrene) (poly(VAc-*b*-St)) by telomerization of vinyl acetate (VAc) with CCl₄ followed by ATRP of styrene.^{20,22} Destarac *et al.* also reported the synthesis of poly(VAc-*b*-St) by con-



Scheme I. Mechanism of ATRP.

*e-mail : cgcho@hanyang.ac.kr

1598-5032/12/339-06 © 2002 Polymer Society of Korea

secutive radical telomerization with chloroform as a telogen and ATRP.^{21,23}

In this research, we used convenient radical polymerization and ATRP methods to prepare the corresponding block copolymer precursor, and prepared block copolymer poly(VA-*b*-St) by subsequent saponification reaction. In order to improve the stability of micelle in solution and the strength of composite materials, we chose vinyl pivalate (VPi) as a monomer. Because of its larger pivalate group, the corresponding polymer has higher syndiotacticity than VAc.^{24,25} Also, poly(VPi-*b*-St) has potentially labile geminal dichloride group -CCl₂- at the junction point between the two blocks. Therefore, another objective of this research is to check whether this bond is stable enough to withstand the saponification reaction.

Experimental

Materials. Vinyl pivalate (VPi) (Aldrich, 99%) was purified as follows: vinyl pivalate were washed with 25% NaHSO₃ aqueous solution. Then, the monomer is washed four times with distilled water, and dried over anhydrous CaCl₂. It is distilled under reduced pressure at 40 °C and stored in a freezer. Styrene (St, Kanto Chemical Co., Ltd, 99%) was purified by passing through an alumina column to remove inhibitor. Copper(I) chloride was purified according to the literature procedure.²¹ CCl₄ (Samchun pure chemical Co., Ltd, 99%) was distilled before use. 2,2-Azobisisobutyronitrile (AIBN) (Wako pure chemical Ind., 98%) was recrystallized from methyl alcohol. Acetone (Samchun pure chemical Co., Ltd, 99%), tetrahydrofuran (Samchun pure chemical Co., Ltd, 99%), 2,2-bipyridyl(Kanto chemical Co., Ltd, 99%), DMSO (Samchun pure chemical Co., Ltd, 98%), and *n*-hexane (Duksan pure chemical Co., Ltd, 96%) were used as received.

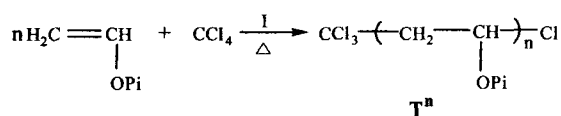
Synthesis of Block Copolymer. Poly(VA-*b*-St) block copolymer was synthesized by following the three-step procedures as shown in Scheme II²¹: (1) radical telomerization of VPi with carbon tetrachloride; (2) ATRP of styrene using the VPi telomer as a macroinitiator; (3) saponification of poly(VPi-*b*-St).

Telomerization. VPi 25 mL (0.17 mole), acetone 25 mL, AIBN (initiator) 27.8 mg (0.17 mmole), CCl₄ 0.49 mL (5.1 mmole) were added into a one-neck round-bottom flask and degassed by flushing with nitrogen. Then, the flask was placed in an oil bath at 50 °C. After reacting 6 h, the unreacted monomer was removed with rotary evaporator. The remaining polymer was purified by precipitation of acetone solution into CH₃OH-H₂O (4:1,v/v), filtered, washed with CH₃OH-H₂O (4:1,v/v), and dried under vacuum. The monomer conversion was determined by gravimetry (yield 9.04 g, 41.8%, white powder). The molecular weight and polydispersity of the telomer were $M_{n,GPC} = 4,540$, $M_{n,NMR} = 4,760$, and $M_w/M_n = 1.55$, respectively.

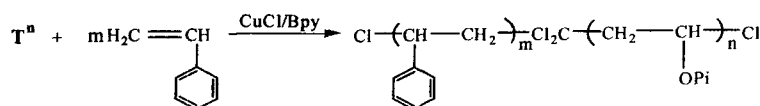
ATRP. Predetermined amounts of copper(I) chloride, macroinitiator (above telomer), styrene were introduced into a 50 mL of round-bottom flask and flushed with nitrogen for 20 min. Then, 2,2-bipyridyl was added and flushed with nitrogen for another 20 min. The flask was placed in a preheated oil bath at 130 °C. After reacting, the copolymer was recovered by precipitation of THF solution into CH₃OH-H₂O (4:1,v/v), filtered, washed with CH₃OH-H₂O, and dried under vacuum. The styrene conversion was determined by gravimetry. The obtained block copolymer was dissolved in THF and passed through an alumina column to remove metal-catalyst. The block copolymer was purified again by precipitation in CH₃OH-H₂O (4:1,v/v).

Saponification. The block copolymer was saponified by a method developed for PVPi.^{24,26} In a 250 mL flask equipped

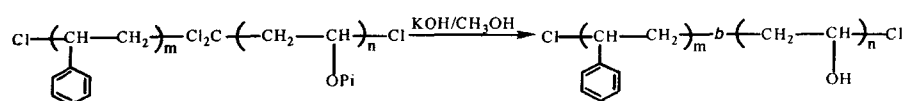
Telomerization



ATRP



Saponification



Scheme II. The synthesis of poly(VA-*b*-St).

with a reflux condenser and dropping funnel, 2.0 g of block copolymer were dissolved in 100 mL of THF. With stirring, 8 mL of 25% KOH methanol solution was added gradually to the copolymer solution and the mixture was kept at 60 °C for 15 min under nitrogen atmosphere. After reaction, excess THF was rotary evaporated and remaining solution was precipitated into CH₃OH. The obtained copolymer was filtered, washed with methanol, water, and dried under vacuum (yield 1.71 g, yellow powder).

Acetylation of Poly(VA-*b*-St).²⁷ 0.5 g of poly(VA-*b*-St), 1 mL of pyridine, 5 mL of acetic anhydride, 5 mL of acetic acid and 10 mL of DMSO were added into an one-neck flask and the mixture was stirred at 100 °C for 24 h under nitrogen. Then the mixture was poured into cool water and the product poly(VAc-*b*-St) was precipitated, and filtered. The copolymer was purified again by reprecipitation of the THF solution into *n*-hexane, and dried under vacuum at 60 °C (yield 0.53 g, 96%, brown powder).

Measurements. The molecular weights and the molecular weight distribution of the pure telomer and the block copolymers were measured by Gel Permeation Chromatography (GPC) equipped with a Waters 717 plus Autosampler, Waters 515 HPLC pump, Waters 410 refractive index detector, and Waters styragel[®] HR series (eluent: THF 35 °C, flow rate: 0.3 mL/min). Polystyrene standards were used to calibrate the columns. The number-average degree of polymerization of the telomer and the block copolymers were also determined using VARIAN 300 MHz UNITY INOVA ¹H-NMR spectrometer, with CDCl₃ or DMSO-*d*₆ as the solvent. The changes of the functional groups of the block copolymers were monitored using a MAGNA-IR760 spectrometer.

Results and Discussion

Telomerization of VPI with CCl₄. The structure of PVPi prepared with CCl₄ and AIBN was analyzed by ¹H-NMR spectroscopy^{20,21} as shown in Figure 1. The signals at 2.8-3.2 ppm(a) and 5.2-5.5 ppm(b) correspond to the methylene and methine protons adjacent to the trichloromethyl group at the α-end, respectively. The resonance at 6.25-6.5 ppm(f) corresponds to methine proton adjacent to terminal chlorine at the ω-end. The peak integration ratio of methine proton at the ω-end to the protons at the α-end is about f/b/a = 0.9/1/2, indicating the presence of both trichloromethyl and chlorine end groups on a polymer chain. Using the ratio of the area of the two peaks (d/a), the number-average molecular weight ($M_{n,NMR}$) by ¹H-NMR was determined, which is close to the GPC value ($M_{n,GPC}$) calibrated against polystyrene standards ($M_{n,GPC} = 4,540$, $M_{n,NMR} = 4,760$).

The number-average molecular weight and conversion were reduced along with the ratio of CCl₄ to VPI increase, which corresponds to Mayo equation and indicate that the quantity of CCl₄ can adjust the molecular weight of the telomers with chain transfer constant $C_{tr} = 1.16$ at 50 °C.²⁸

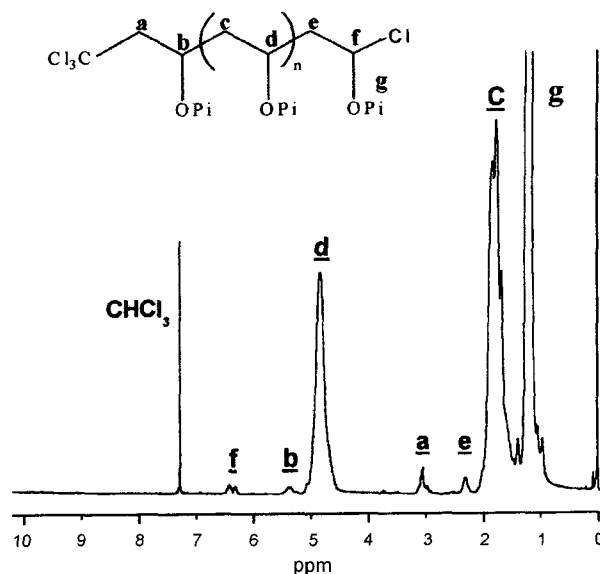


Figure 1. ¹H-NMR spectrum of PVPi prepared using CCl₄ as a telogen and AIBN as an initiator.

Because of using CCl₄ with a chain transfer constant $C_{tr} \sim 1$, obtained polymers have relatively low molecular weight distribution ($M_w/M_n = 1.55$) and predictable molecular weights compared to CHCl₃.²⁰⁻²² Thus, it appeared from our experiments and structural analysis that the polymerization with AIBN and CCl₄ initiating system was well controlled.

ATRP of Styrene Initiated by PVPi-Cl Telomer. The obtained PVPi telomer from the solution polymerization is used as a macroinitiator in ATRP of styrene. Literature show that 1,1,1-trichloroalkanes, RCCl₃, are efficient initiators for Cu-catalyzed ATRP of St.^{11,16,21-23,29} Although the electronic effect of the R and R' groups in the CCl₃R''-R'-RCl have influence on the reactivity of the two end groups,^{11,29} trichloromethyl end group in the PVPi telomer is more efficient initiator for Cu-catalyzed ATRP compared to monochloride end group.^{22,23,29}

Figure 2 shows the time-conversion curve and the semi-logarithmic kinetic curve of the styrene polymerization, which was initiated by macroinitiator PVPi-Cl/CuCl/Bpy. The conversion gradually increased until the polymerization reached 44% monomer conversion, and then the polymerization rate dropped abruptly, which was similar with the result reported by Matyjaszewski *et al.*²² The apparent polymerization rate is first order with respect to monomer, and a deviation occurred from theory at higher conversions. Figure 3 shows the number-average molecular weight versus conversion curve. It shows a linear increase of molecular weight with monomer conversion. In addition, the molecular weight distribution ($M_w/M_n \sim 1.3-1.4$) of the obtained copolymer is relatively narrow compared to macroinitiator ($M_w/M_n \sim 1.6$) and independent of conversion. Moreover, experimental molecular weights match the theoretical values at low

monomer conversion, which is characteristic of a fast and nearly quantitative initiation. At higher conversions, M_n values are lower than theoretical values probably due to a difference in hydrodynamic volume between polystyrene standard and the diblock copolymer.²¹ The additional indication of the block copolymer formation is given by Figure 4, representing an overlay of GPC traces of the PVPI-Cl macroinitiator and the resulting polymer. The complete consumption of the macroinitiator and the shift of chromatograms towards high molecular weights support the formation of a block copolymer.

Figure 5 represents ¹H-NMR spectrum of the block copoly-

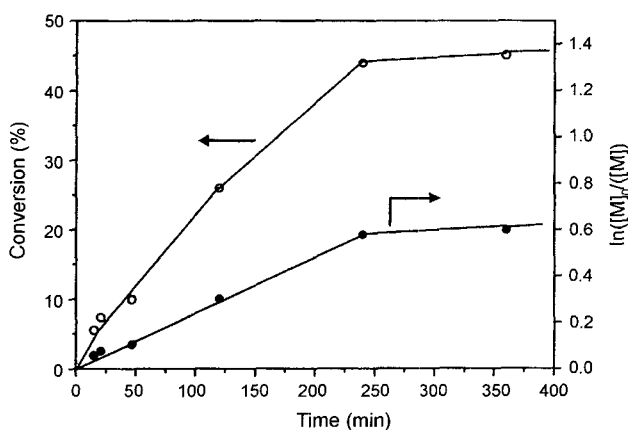


Figure 2. Kinetic plot for ATRP of styrene initiated by PVPI-Cl telomer and catalyzed by CuCl/2,2'-bipyridine {[St] = 8.7 M, [Macroinitiator]/[CuCl]/[Bpy]/[St] = 1 : 1 : 2.0 : 300, 130 °C}. Conversion(%) = (Product weight - Macroinitiator weight) / St weight × 100%.

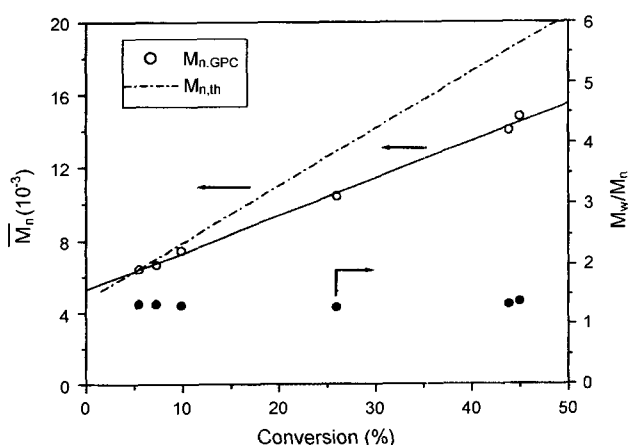


Figure 3. Dependence of number-average molecular weight ($M_{n,GPC}$, $M_{n,th}$) and polydispersity (M_w/M_n) on styrene conversion in bulk ATRP of styrene initiated by PVPI-Cl telomer and catalyzed by CuCl/2,2'-bipyridine {[St] = 8.7 M, [Macroinitiator]/[CuCl]/[Bpy]/[St] = 1 : 1 : 2.0 : 300, 130 °C}. $M_{n,th} = ([St]_0/[Macroinitiator]_0) \times MSt \times Conversion(\%) + (M_n)_{Macroinitiator}$.

mer at 45% monomer conversion. From the spectrum, it is possible to calculate the block length of polystyrene, and the obtained value matches well with the $M_{n,th}$ result ($M_{n,NMR} = 17,550$; $M_{n,GPC} = 14,730$; $M_{n,th} = 18,800$).

Saponification and Acetylation of the Diblock Copolymer. Poly(VPI-*b*-St) was saponified and the resultant poly(VA-*b*-St) was analyzed by ¹H-NMR. Figure 6 shows the absence of the pivaloyl proton peak at 1.1 ppm, indicates that PVPi block had been almost saponified. From the ¹H-NMR spectrum for poly(VA-*b*-St) block copolymer, the estimated tacticities from the three OH peak at 4.1-4.7 ppm^{24,25} are 55.6% (use deconvolution method) for syndiotactic diad. Figure 7 shows the ¹H-NMR spectrum of the poly(VAc-*b*-St) after acetylation of poly(VA-*b*-St). Compared to poly(VA-*b*-St), the ¹H-NMR spectrum of the poly(VAc-*b*-St) shows

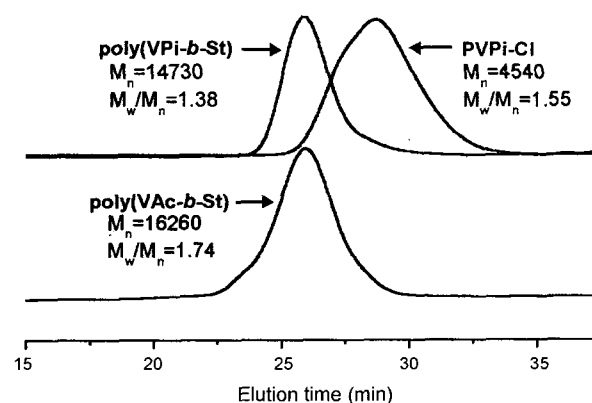


Figure 4. GPC traces of macroinitiator and diblock copolymers.

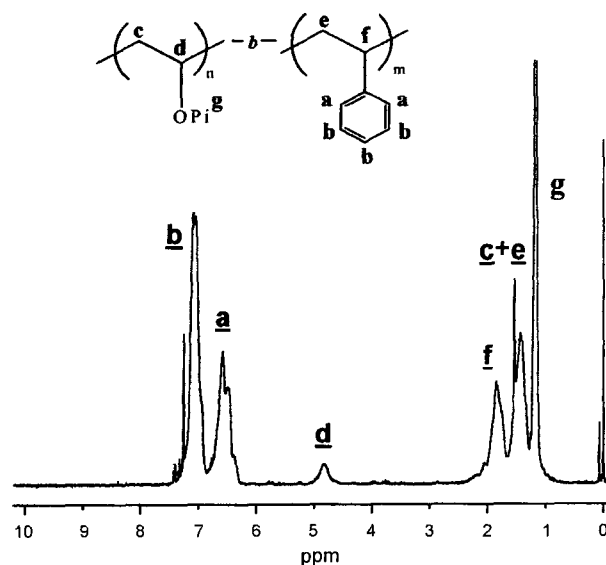


Figure 5. ¹H-NMR spectrum of poly(VPI-*b*-St). Polymerization conditions: {[St] = 8.7 M, [Macroinitiator]/[CuCl]/[Bpy]/[St] = 1 : 1 : 2.0 : 300, time = 6 h, temp. 130 °C, conversion = 45%}.

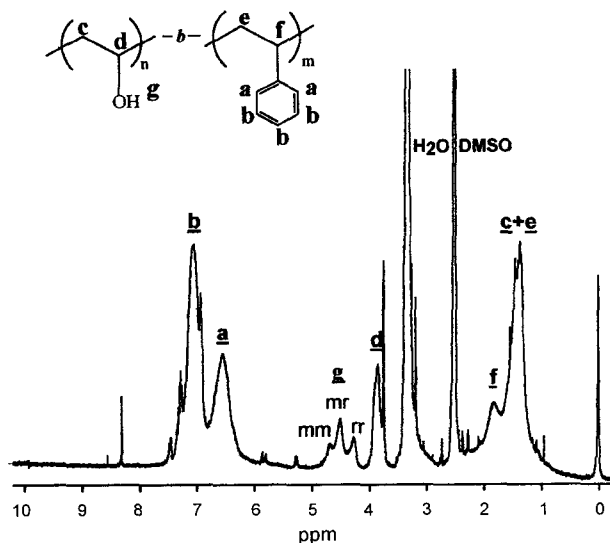


Figure 6. $^1\text{H-NMR}$ spectrum of poly(VA-*b*-St) prepared by the saponification of poly(VPI-*b*-St).

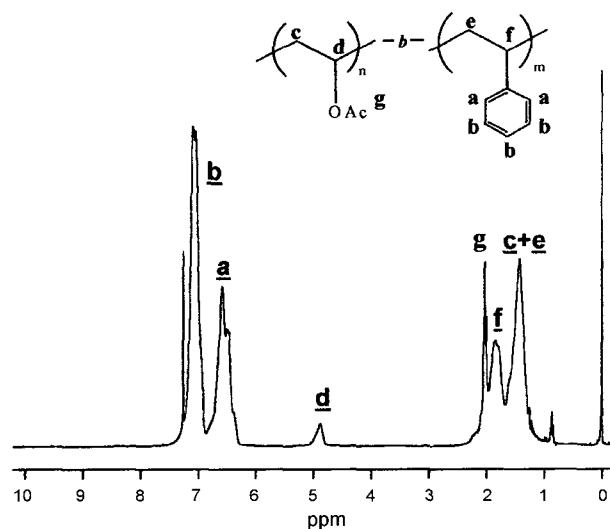


Figure 7. $^1\text{H-NMR}$ spectrum of poly(VAc-*b*-St) prepared by the acetylation of poly(VA-*b*-St).

that original OH and CH-OH peak (3.8 ppm) disappeared whereas CH-OAc peak appeared, which indicate that vinyl alcohol was acetylated. The 0.9 ppm peak in the Figure 7 is methyl proton peak of *n*-hexane persisted in the polymer, which was used for precipitation of the polymer.

Figure 8 shows the IR spectra of three diblock copolymers. poly(VPI-*b*-St) spectrum shows carbonyl peak at 1740 cm^{-1} , -C-O- and -O-C- peak in the ester groups about 1150 cm^{-1} and 1280 cm^{-1} , respectively, and *tert*-butyl peak at 1365 cm^{-1} and 1390 cm^{-1} ; poly(VA-*b*-St) spectrum shows OH peak at $3550\text{--}3230\text{ cm}^{-1}$, whereas carbonyl peak, -C-O peak in the

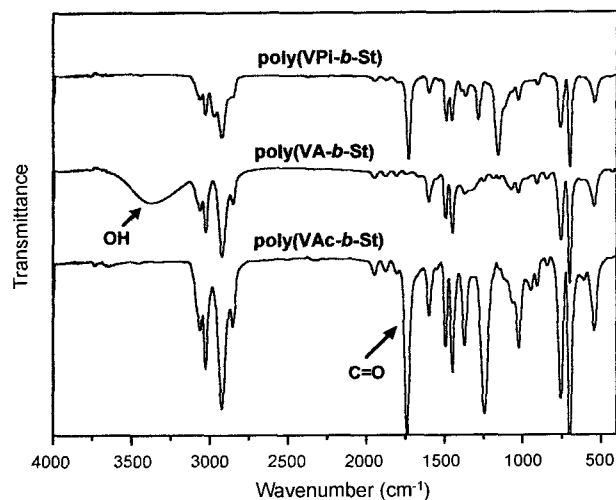


Figure 8. FT-IR spectra of three diblock copolymers.

ester group and *tert*-butyl peak disappeared; Poly(VAc-*b*-St) spectrum shows again carbonyl peak at 1740 cm^{-1} , -C-O- and O-CH₃ in the ester groups at 1020 and 1240 cm^{-1} , respectively, whereas OH peak disappeared. Also, all spectra show the presence of polystyrene block (benzene ring C-H at 3100 cm^{-1} , C=C at 1600 cm^{-1}) in the block copolymers.

Figure 4 shows the GPC traces of two diblock copolymers poly(VPI-*b*-St) and poly(VAc-*b*-St). After saponification and acetylation, the GPC traces shows the almost identical shape, which indicate that the block copolymer is stable under the saponification and acetylation, i.e., the geminal dichloride junction point of the block copolymer is not involved in the cleavage reaction under the saponification condition. In order to survey whether the central geminal dichloride -CCl₂- in the poly(VPI-*b*-St) undergoes substitution or elimination reaction under the saponification condition, we used $^{13}\text{C-NMR}$ analysis for the poly(VA-*b*-St), but -CCl₂- peak (about 81 ppm) is not seen on the spectrum. Destarac *et al.* showed that the central -CCl₂- quaternary carbon in oligostyrene sample does not show any signal on $^{13}\text{C-NMR}$ spectra, presumably because of its much longer relaxation time compared to that of terminal carbon atoms.²⁹ Therefore, the reaction of the central geminal dichloride needs further study. The slight increase of the $M_{n,GPC}$ value of poly(VAc-*b*-St) is believed to be originated from the reprecipitation procedure, and the reason of slight broadening of the MWD is unclear yet.

Conclusions

Well-defined amphiphilic diblock copolymer with both high syndiotactic (55.6%) hydrophilic segments (PVA) and hydrophobic segments (PSt) was synthesized by consecutive telomerization, ATRP, and saponification. By varying the $[\text{CCl}_4]/[\text{VPI}]$ ratio and the reaction time with styrene in the

telomerization and ATRP steps, respectively, the chain length of both blocks are easily controlled. Therefore, a wide range of molecular weights and copolymer compositions can be achieved by this method. In the saponification of poly(VPi-*b*-St) and acetylation of poly(VA-*b*-St), the diblock copolymers main chain was stable, which is confirmed by GPC data of the poly(VAc-*b*-St) and IR data of the diblock copolymers.

Acknowledgement. This research was supported by the Center for Advanced Functional Polymers and BK21.

References

- (1) F. J. Baltá Calleja and Z. Roslaniec, *Block Copolymers*, Marcel Dekker, Inc., New York, 2000, pp 1-5, pp 531-572.
- (2) Z. J. Lu, X. Y. Huang, and J. L. Huang, *J. Polym. Sci., Polym. Chem. Ed.*, **37**, 2595 (1999).
- (3) Z. J. Lu, X. Y. Huang, and J. L. Huang, *J. Polym. Sci., Polym. Chem. Ed.*, **36**, 109 (1998).
- (4) R. Saito, S. Okamura, and K. Ishizu, *Polymer*, **36**, 4515 (1995).
- (5) R. Saito, S. Okamura, and K. Ishizu, *Polymer*, **37**, 5255 (1996).
- (6) J. M. Park, *Korea Polym. J.*, **9** (1), 51 (2001).
- (7) S. H. Kim and W. H. Jo, *Korea Polym. J.*, **9** (4), 185 (2001).
- (8) T. Otsu, T. Matsunaga, T. Doi, and A. Matsumoto, *Eur. Polym. J.*, **31**, 67 (1995).
- (9) R. Saito, S. Yoshida, and K. Ishizu, *J. Appl. Polym. Sci.*, **63**, 849 (1997).
- (10) K. Matyjaszewski, *Controlled Radical Polymerization*, ACS Symposium Series 685, American Chemical Society, Washington, DC., 1998.
- (11) K. Matyjaszewski, *Controlled/Living Radical Polymerization*, ACS Symposium Series 768, American Chemical Society, Washington, DC., 2000.
- (12) T. E. Patten and K. Matyjaszewski, *Adv. Mater.*, **10**, 901 (1998).
- (13) J.-S. Wang and K. Matyjaszewski, *J. Am. Chem. Soc.*, **117**, 5614 (1995).
- (14) M. Kato, M. Kamigaito, M. Sawamoto, and T. Higashimura, *Macromolecules*, **28**, 1721 (1995).
- (15) T. Ando, M. Kato, M. Kamigaito, and M. Sawamoto, *Macromolecules*, **29**, 1070 (1996).
- (16) C. Granel, Ph. Dubois, R. Jérôme, and Ph. Teyssié, *Macromolecules*, **29**, 8576 (1996).
- (17) V. Percec and B. Barboiu, *Macromolecules*, **28**, 7970 (1995).
- (18) D. M. Haddleton, C. B. Jasieczek, M. J. Hannon, and A. J. Shooter, *Macromolecules*, **30**, 2190 (1997).
- (19) M. Destarac, J.-M. Bessière, and B. Boutevin, *Macromol. Rapid Commun.*, **18**, 967 (1997).
- (20) J. H. Xia, H. J. Paik, and K. Matyjaszewski, *Macromolecules*, **32**, 8310 (1999).
- (21) M. Destarac and B. Boutevin, *Macromol. Chem. Phys.*, **201**, 1189 (2000).
- (22) H. J. Paik, M. Teodorescu, J. H. Xia, and K. Matyjaszewski, *Macromolecules*, **32**, 7023 (1999).
- (23) M. Destarac, J.-M. Bessière, and B. Boutevin, *Polymer Prepr.*, **38**(1), 677 (1997).
- (24) T. Yamamoto, R. Fukae, T. Saso, O. Sangen, M. Kamachi, T. Sato, and Y. Fukunishi, *Polym. J.*, **24**(1), 115 (1992).
- (25) W. S. Lyoo, J. Blackwell, and H. D. Ghim, *Macromolecules*, **31**, 4253 (1998).
- (26) T. Yamamoto, S. Yoda, H. Takase, T. Saso, O. Sangen, R. Fukae, M. Kamachi, and T. Sato, *Polym. J.*, **23**, 185 (1991).
- (27) T. Yamamoto, S. Seki, R. Fukae, O. Sangen, and M. Kamachi, *Polym. J.*, **22**, 567 (1990).
- (28) D. K. Kim and C. G. Cho, *Polymer (Korea)*, in press.
- (29) M. Destarac, J.-M. Bessière, and B. Boutevin, *J. Polym. Sci., Polym. Chem. Ed.*, **36**, 2933 (1998).