

## Synthesis and Characterization of Low Molecular Weight Poly(methyl acrylate)-*b*-Polystyrene by a Combination of ATRP and Click Coupling Method

Aleya Hasneen, Su Jeong Kim, and Hyun-jong Paik\*

Department of Polymer Science and Engineering, Pusan National University, Busan 609-753, Korea

Received April 26, 2007; Revised August 6, 2007

**Abstract:** The combination of atom transfer radical polymerization (ATRP) and click chemistry was employed for the efficient preparation of well-defined block copolymers. Bromo terminated poly(methyl acrylate) (pMA-Br) was prepared by an ATRP initiator, ethyl-2-bromoisobutyrate (EBiB). Subsequently, the bromine chain end of pMA-Br was converted to an azide group by simple nucleophilic substitution reaction.  $\alpha$ -Alkyn- $\omega$ -bromo-functionalized polystyrene was also synthesized by ATRP using the alkyn-functionalized initiator, propargyl-2-bromoisobutyrate (PGBiB). In both cases, the conversion was limited to a low level to ensure a high degree of chain end functionality. Then the coupling reaction between the azide end group in pMA-N<sub>3</sub> and alkyn-functionalized PGBiB-pSt was performed by Cu(I) catalysis. This coupling reaction was monitored by gel permeation chromatography (GPC). The synthesized block copolymer was characterized by FT-IR, <sup>1</sup>H-NMR spectroscopy and <sup>1</sup>H-<sup>1</sup>H COSY correlation spectroscopy.

**Keywords:** ATRP, click-coupling reaction, poly(methyl acrylate)-*b*-polystyrene, block copolymers.

### Introduction

Block copolymers are recognized as smart polymeric materials because of their crucial roles in various fields such as nanotechnology as well as advanced technology. Recently, block copolymers are being widely used as information storage, drug delivery and photonic crystals.<sup>1</sup> In this context, to make well defined block copolymers by convenient method is particularly important.

In the past decade, the development of living radical polymerizations (LRP) allows the synthesis of copolymers not only with a predetermined degree of polymerization and narrow molecular weight distribution (low polydispersity,  $M_w/M_n$ ) but also with high functionality.<sup>2</sup> One of the most efficient LRP methods is atom transfer radical polymerization (ATRP).<sup>3-10</sup> The polymers produced by ATRP preserve the terminal halogen atom(s) and can be successfully converted to various end groups through appropriate transformation, especially nucleophilic substitution.<sup>11</sup> For instance, the substitution of a halogen atom from a polymer chain end by an azide anion is very efficient.<sup>12,13</sup> This chain-end functionality can be used to make numerous types of polymeric structures such as block copolymers using ATRP and click coupling method.

During the last two years, click reaction has attained a

great deal of attention due to their high specificity, quantitative yields, and near-perfect fidelity in the presence of most functional groups. The most popular click chemistry reaction is the copper-catalyzed Huisgen dipolar cycloaddition reaction between an azide and an alkyn leading to 1,2,3-triazole under moderate reaction condition.<sup>14-16</sup> In the field of materials chemistry, this reaction has been utilized to functionalize carbon nanotubes,<sup>17</sup> and polymers,<sup>18-20</sup> as well as to prepare dendrimers,<sup>21-23</sup> shell cross-linked nanoparticles,<sup>24</sup> stars polymers,<sup>25</sup> macrocyclic polymers,<sup>26</sup> and block copolymers.<sup>27-29</sup> In 2005 van Hest *et al.* first synthesized different di-block copolymers using click coupling method from polystyrene (pSt), poly(methyl methacrylate) (pMMA) and poly(ethylene glycol) (PEG) prepared by ATRP. The clickable functions were subsequently obtained by chemical reaction onto the chain end groups. Hizal *et al.* in 2006 synthesized block copolymers from pSt, pMMA, PEG, and poly(*tert*butyl acrylate) (ptBA) using the same strategy. All polymers, except the PEG, were prepared by ATRP and chain end groups were subsequently modified to introduce an anthracene and maleimide functions in order to perform Diels-Alder (DA) reactions. Recently Martina H. Stenzal *et al.* synthesized well defined poly(vinyl acetate) (pVAc) containing polystyrene block copolymer (pSt-*b*-pVAc) using RAFT and click coupling approach with different molecular weight. Two different RAFT agents azido xanthate, 3-azidopropyl 2-bromoethanoate and acetylene-dithiobenzoate

\*Corresponding Author. E-mail: hpaik@pusan.ac.kr

agent were synthesized to make these block copolymers.

Here, we report the synthesis and characterization of low molecular weight pMA-*b*-pSt using click coupling approach. The objective of the study was to thoroughly characterize the pMA-*b*-pSt di-block copolymer synthesized by ATRP and click coupling method. FT-IR, <sup>1</sup>H-NMR and two dimensional <sup>1</sup>H-<sup>1</sup>H COSY spectroscopic techniques were used to characterize the structure of this block copolymer. Two dimensional <sup>1</sup>H-<sup>1</sup>H COSY NMR data suggests the formation of block copolymer by correlating the protons and also indicates triazole unit as a result of click coupling reaction. The work also includes an investigation of the click coupling reaction via GPC monitoring by the consumption of alkyn functionalized PgBiB-pSt with time as a result of coupling with azide functionalized pMA-N<sub>3</sub>.

## Experimental

**Materials.** Methyl acrylate (Junsei, 99.5%) and styrene (Junsei, 99.5%) were distilled over CaH<sub>2</sub> and stored in a refrigerator under nitrogen. CuBr (Aldrich, 98%) was purified according to the literature.<sup>30</sup> Ethyl 2-bromoisobutyrate (EBiB) (Aldrich, 98%) and *N,N,N',N'',N'''*-pentamethyl diethylenetriamine (PMDETA) (Aldrich, 98%) were purified through vacuum distillation. 2,2'-Bipyridyl (Bipy) (Aldrich, 99%), 2-bromoisobutyryl bromide (Aldrich, 98%), sodium azide (NaN<sub>3</sub>) were used as received.

**Synthesis of Propargyl 2-Bromoisobutyrate (PgBiB).** The initiator containing alkyn functionality was synthesized according to the literature.<sup>31</sup> The yield was 52%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>); δ 1.95 (s, 6H), 2.51(t, 1H), 4.77 (d, 2H); IR (neat) 3296, 2132, 1741 cm<sup>-1</sup>.

**Synthesis of PgBiB-pSt.** α-alkyn ω-bromo functionalized polystyrene (PgBiB-pSt) was synthesized with conditions modified from previously reported methods.<sup>32</sup> A mixture of styrene (4 mL, 34.7 mmol), anisole (0.4 mL), PMDETA (150 μL, 0.722 mmol) was deoxygenated in a dry Schlenk flask by four freeze-pump-thaw cycle. The contents were again frozen and CuBr (51.8 mg, 0.36 mmol), CuBr<sub>2</sub> (8.0 mg, 0.036 mmol) were added. The freeze-pump-thaw cycle was repeated two more times, and the mixture was allowed to melt. The Schlenk flask was immersed in an oil bath with preset temperature at 110 °C and initiator PgBiB (105 μL, 0.722 mmol) was added using N<sub>2</sub> purged syringe. 0.5 mL of the reaction aliquot was taken immediately as a reference sample for GC analysis. After certain interval, 0.5 mL of the reaction aliquot was taken under N<sub>2</sub> atmosphere and diluted with 1 mL THF. The polymerization was stopped after 4 h. The mixture was diluted with THF and passed through a neutral alumina column to remove the catalyst. The polymer was isolated by precipitation from methanol.

**Synthesis of pMA-Br.** Bromo end functionalized poly (methyl acrylate) (pMA-Br) was synthesized according to the literature under modified conditions.<sup>33</sup> In a dry Schlenk

flask, MA (4 mL, 44.4 mmol), anisole (0.4 mL) PMDETA (158 μL, 0.765 mmol), were added and deoxygenated followed by four freeze-pump-thaw cycle. The contents were again frozen and CuBr (51.7 mg, 0.382 mmol), CuBr<sub>2</sub> (8.5 mg, 0.038 mmol) were added. The freeze-pump-thaw cycle was repeated two more times, and the mixture was allowed to melt. The Schlenk flask was immersed in an oil bath with preset temperature at 70 °C and initiator EBiB (113 μL, 0.765 mmol) was added using N<sub>2</sub> purged syringe. 0.5 mL of the reaction aliquot was taken immediately as a reference sample for GC analysis. At timed interval, 0.5 mL of the reaction aliquot was taken under N<sub>2</sub> atmosphere and diluted with 1 mL THF. The polymerization was stopped after 2 h at low monomer conversion to retain high degree of bromine chain end functionality. The mixture was diluted with THF and passed through a neutral alumina column to remove the catalyst. The polymer was isolated by precipitation from methanol-water mixture (1 : 1 v/v). The polymer was dried under vacuum.

**Synthesis of Azido-Terminated Poly(methyl acrylate).** The bromo terminated pMA-Br (0.18 mmol) was reacted with NaN<sub>3</sub> (0.20 mmol) for 3 h at room temperature in DMF (3 mL) to yield azido terminated polymer (pMA-N<sub>3</sub>). The polymer was isolated by removal of the solvent under vacuum and precipitation from methanol-water mixture. The azido terminated polymer (pMA-N<sub>3</sub>) was dried under vacuum.

**Synthesis of Block Copolymer via Azide-Alkyn Coupling.** In a flask, azido terminated pMA-N<sub>3</sub> (0.30 mmol), alkyn functionalized pSt (0.49 mmol), bipyridine (2.40 mmol) and 3 mL THF were added. The solution was purged with nitrogen and degassed using four freeze-pump-thaw cycle and then CuBr (0.30 mmol) was added. The mixture turned into homogeneous reddish brown solution and set into oil bath at 35 °C under stirring condition. The initial sample was taken as a reference and other samples also were taken every after 2 h to monitor click coupling reaction by GPC. After 24 h the final mixture was diluted in THF and passed through short alumina column in order to remove copper catalyst. The solvent was concentrated by rotary evaporation and polymer was isolated by precipitation from methanol.

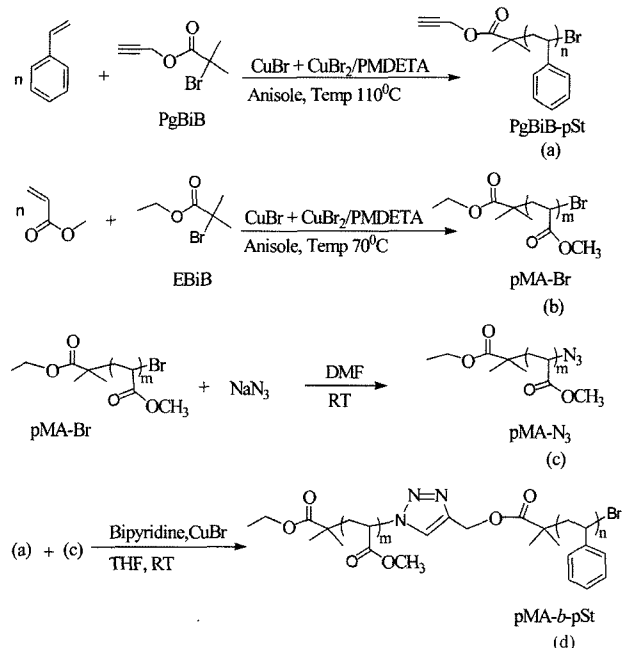
**Characterization.** Molecular weight and molecular weight distribution ( $M_w/M_n$ ) were determined using gel permeation chromatography (GPC) calibrated with polystyrene standards and equipped with Agilent 1100 pump, RID detector and SDV 5 μm 10<sup>5</sup>, 10<sup>3</sup>, 10<sup>2</sup> Å 8.0 × 300.0 mm columns. Monomer conversion was determined by HP 5890 gas chromatography equipped with HP101 column (Methyl Silicone Fluid, 25 m × 0.3 mm × 0.3 μm) and FID detector. Fourier-transform infrared (FT-IR) spectra were recorded on Spectrum GX, Perkin Elmer. <sup>1</sup>H-NMR spectra were obtained on a Varian Plus 300 spectrometer. Two dimensional <sup>1</sup>H-<sup>1</sup>H correlation spectroscopy were conducted in CDCl<sub>3</sub> with an Inova 500 MHz spectrometer.

## Results and Discussion

The synthetic scheme used to prepare block copolymer poly(methyl acrylate)-*b*-polystyrene (pMA-*b*-pSt) is shown in Scheme I. Low molecular weight homopolymer poly(methyl acrylate) (pMA-Br) was synthesized and  $\alpha$ -alkyn,  $\omega$ -bromo functionalized polystyrene (PgBiB-pSt) was also prepared from alkyne functionalized initiator (PgBiB) using standard technique developed by Matyjaszewski and co-workers.<sup>4</sup> The bromine chain end of pMA-Br was replaced into azide group using  $\text{NaN}_3$  in DMF through nucleophilic substitution reaction.<sup>34</sup> Subsequently block copolymer (pMA-*b*-pSt) was synthesized employing click coupling method<sup>35</sup> through combination of azido group in pMA- $\text{N}_3$  with PgBiB-pSt.

The chain end functionality of polymer can also be modified by post-polymerization modification. In both polymerizations, we added  $\text{CuBr}_2$  as an additional deactivator to reduce the termination reaction through radical-radical coupling.<sup>36</sup> The polymerizations were stopped at relatively low monomer conversion to retain high degree of chain end functionality.<sup>37</sup> Poly(methyl acrylate) (pMA-Br) with bromine chain end was prepared from ATRP with ethyl bromoisobutyrate EBiB as an initiator. Azido terminated poly(methyl acrylate) (pMA- $\text{N}_3$ ) was made by simple nucleophilic substitution with  $\text{NaN}_3$  in DMF at room temperature.

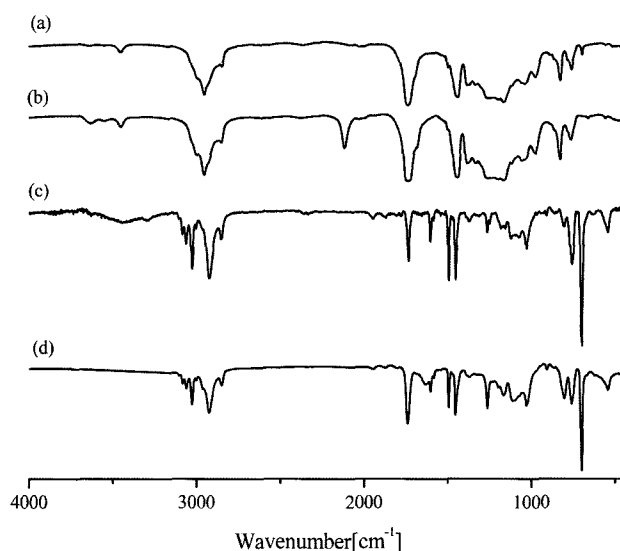
The appearance of intense azide signal at  $2100\text{ cm}^{-1}$  and disappearance of C-Br at  $690\text{ cm}^{-1}$  using IR spectroscopy



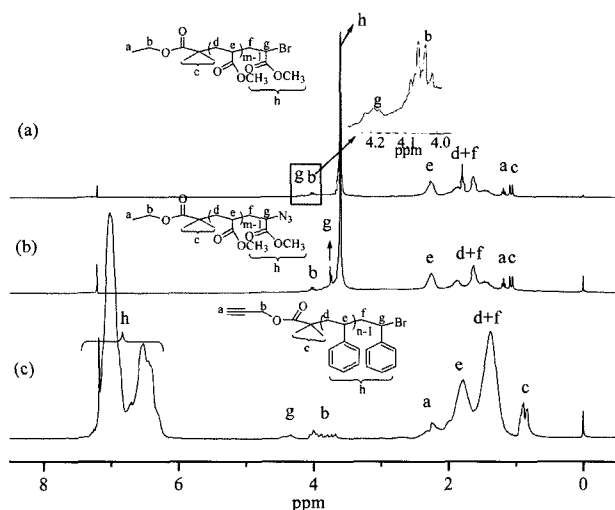
**Scheme I.** (a) Synthesis of  $\alpha$ -alkyn  $\omega$ -bromo functionalized polystyrene PgBiB-pSt, (b) synthesis of bromo functionalized pMA-Br, (c) azide functionalized pMA- $\text{N}_3$ , and (d) subsequent synthesis of block copolymer pMA-*b*-pSt using click coupling method.

indicate the complete conversion of bromo to azide chain end (Figure 1). The  $^1\text{H-NMR}$  spectra of the pMA-Br and pMA- $\text{N}_3$  are shown in Figure 2. Before the substitution reaction, the proton signal of the  $\alpha$  position to the terminal bromine was at 4.12 ppm, whereas that to the terminal azido group after the substitution reaction shifted to 3.74 ppm and no residual peak was found at 4.12 ppm; this suggests that the substitution of azide with bromine was highly efficient.

After nucleophilic substitution of pMA-Br to pMA- $\text{N}_3$ , the molecular weight was almost same as pMA-Br and PDI also remained low which is summarized in Table I. This



**Figure 1.** FT-IR spectra before and after azidation of pMA-Br: (a) pMA-Br, (b) pMA- $\text{N}_3$ , (c) PgBiB-pSt, and (d) click coupled product, pMA-*b*-pSt.



**Figure 2.**  $^1\text{H-NMR}$  spectra before and after end-group transformation of pMA-Br: (a) pMA-Br, (b) pMA- $\text{N}_3$ , and (c) alkyne functionalized PgBiB-pSt.

**Table I.**  $\alpha$ ,  $\omega$  Functionalized Polymers Prepared by ATRP and Post-Polymerization Block Copolymer Prepared by Azide-Alkyn Coupling

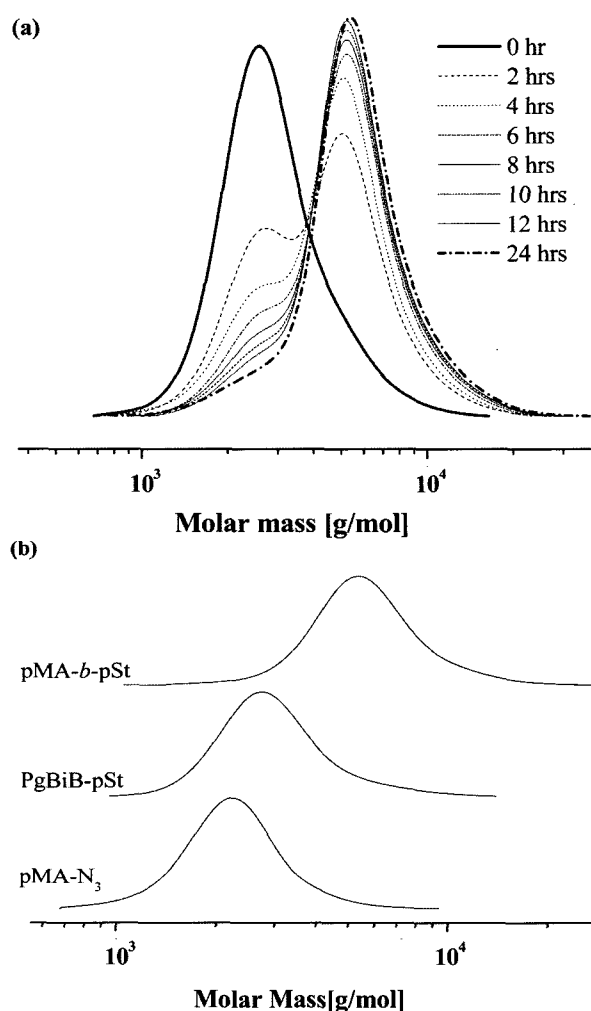
Entry No.	Polymer	Temp. (°C)	Conversion (%)	$M_n$ [g/mol] <sup>a</sup> (Theoretical)	$M_n$ [g/mol] <sup>b</sup> NMR	$M_n$ [g/mol] <sup>c</sup> GPC	$M_w/M_n$
1	PgBiB-pSt	110	60.30	3,200	3,120	3,170	1.09
2	pMA-Br	70	45.50	2,440	2,700	2,410	1.12
3	pMA-N <sub>3</sub>	30	...	2,390	2,640	2,370	1.13
4	pMA- <i>b</i> -pSt	35	...	5,590	6,190	5,490	1.20

1, [Styrene]<sub>0</sub> : [PgBiB]<sub>0</sub> : [CuBr]<sub>0</sub> : [CuBr]<sub>0</sub> : [PMDETA]<sub>0</sub> = 48 : 1 : 0.5 : 0.05 : 1, Anisole (10 vol% to monomer). 2, [MA]<sub>0</sub> : [EBiB]<sub>0</sub> : [CuBr]<sub>0</sub> : [CuBr]<sub>0</sub> : [PMDETA]<sub>0</sub> = 58 : 1 : 1 : 0.05 : 1, Anisole (10 vol% to monomer). 4, [PgBiB-pSt]<sub>0</sub> : [pMA-N<sub>3</sub>]<sub>0</sub> : [CuBr]<sub>0</sub> : [Bipy]<sub>0</sub> = 1.6 : 1 : 1 : 6, THF (solvent). <sup>a</sup>( $[M]_0/[I]_0 \times \text{conversion} \times \text{MW of monomer}$ ) + MW of initiator. <sup>b</sup>Determined by comparing <sup>1</sup>H-NMR peak areas of polymer backbone protons with protons on either  $\alpha$  or  $\omega$  chain terminus. <sup>c</sup>Determined by gel permeation chromatography with conventional calibration based on polystyrene standards.

suggests that the modification of bromine chain into azide chain end was efficient by substitution. Well-defined alkyne functionalized polystyrene with low  $M_w/M_n$  was synthesized using PMDETA/CuBr catalyst and propargyl 2-bromo-isobutyrate (PgBiB) as the initiator. Introduction of alkyne functionality was confirmed by FT-IR as well as <sup>1</sup>H-NMR spectra (Figure 2(c)).

To synthesize block copolymer (pMA-*b*-pSt), Cu(I) catalyzed azide-alkyn [3 + 2] coupling was performed. The click coupling reaction between the azido chain end group in pMA-N<sub>3</sub> with  $\alpha$ -alkyn group in PgBiB-pSt was evaluated by GPC. The GPC curves indicate that the coupling reaction proceeded fast and within 2 h molecular weight shift towards higher molecular weight with consumption of alkyne group as a result of coupling with azido group (Figure 3). It was found from this GPC data that the successive increase of molecular weight and the decrease of  $M_w/M_n$  with time. After 24 h almost monomodal curve appeared instead of bimodal distribution curve as a result of click coupling of alkyne group with azido group. Furthermore, a shift of molecular weight towards the higher value confirms the successful block copolymer formation (Figure 3(b)) and molecular weight matches with the theoretical value (Table I). However, a slight increase of the polydispersity was found after the reaction, which could be ascribed to the presence of remaining homopolymers.

The efficient click coupling between terminal azide end group in pMA-N<sub>3</sub> with alkyne group in PgBiB-pSt was found from spectroscopic analysis such as IR as well as <sup>1</sup>H-NMR. The disappearance of characteristic peak for azide group at 2100 cm<sup>-1</sup> (Figure 1(d)) indicates the successful formation of click coupled copolymer. The <sup>1</sup>H-NMR spectrum of block copolymer (pMA-*b*-pSt) is shown in Figure 4. As a result of click coupling, the new peak appeared at 5.3 ppm for proton from CH<sub>2</sub> near the triazole unit and the proton of the CH on the triazole circle was found at 7.8 ppm. After click coupling, the broad peak was appeared at 3.59-3.74 ppm region for the proton from the backbone (-OCH<sub>3</sub>) group of pMA-N<sub>3</sub>. It is difficult to estimate the consumption of azido group by



**Figure 3.** GPC chromatograms (a) the mixture from click coupling reaction between pMA-N<sub>3</sub> and PgBiB-pSt at 0 time and successive increase of click coupled product, pMA-*b*-pSt with time (b) pMA-N<sub>3</sub>, PgBiB-pSt, and pMA-*b*-pSt.

conventional <sup>1</sup>H-NMR spectroscopy. We used <sup>1</sup>H-<sup>1</sup>H COSY spectroscopy to confirm the successful click coupling reac-

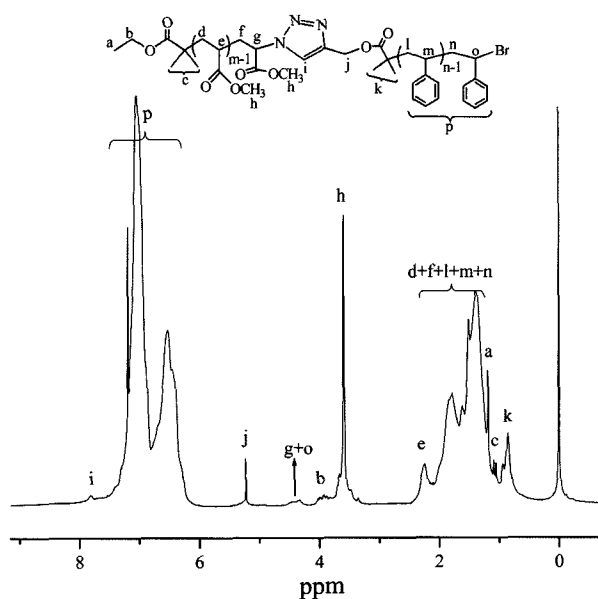


Figure 4.  $^1\text{H-NMR}$  spectrum of click coupled product, pMA-*b*-pSt.

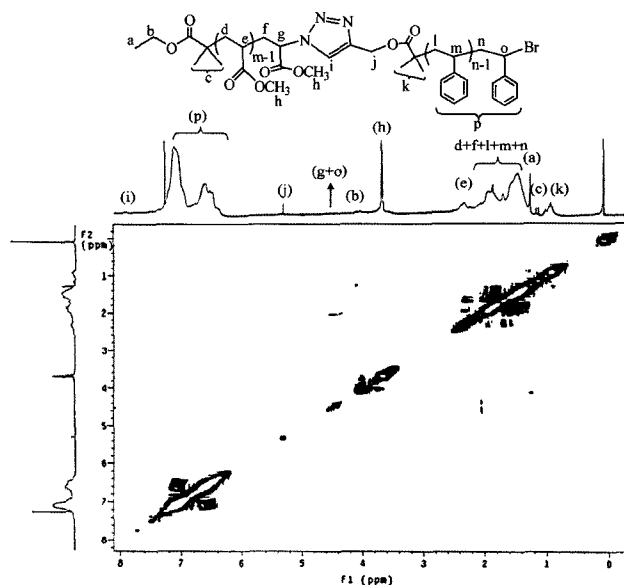


Figure 5. COSY spectrum and peak assignments for block copolymer pMA-*b*-pSt. No correlation signals of pMA(H)- $\text{N}_3$  at 3.74 ppm with the adjacent terminal unit backbone methylene proton at 1.84 ppm indicates complete consumption of azido group as a result of click coupling. Off-diagonal correlation peaks at 4.5 ppm and 2 ppm indicate coupling between the terminal methine proton pMA(H)-acrylate and adjacent terminal unit backbone methylene protons.

tion.<sup>38</sup> The absence of off-diagonal cross-peaks indicative of correlation of the terminal methine pMA(H)- $\text{N}_3$  at 3.74 ppm with the adjacent terminal unit backbone methylene protons at 1.84 ppm, suggests the azido terminated polymer is com-

pletely consumed as a result of click coupling. Off-diagonal correlation peaks at 4.5 ppm and 2 ppm indicate coupling between the terminal methine proton pMA(H)-acrylate and adjacent terminal unit backbone methylene protons.

## Conclusions

Well-defined block copolymer pMA-*b*-pSt was synthesized by combining the  $\omega$ -azido end in pMA- $\text{N}_3$  with  $\alpha$ -alkyn functionalized PgBiB-pSt via a Huisgen 1,3 dipolar click cycloaddition reaction. FT-IR and  $^1\text{H-NMR}$  analysis confirm the successful click coupling between azide chain end of pMA- $\text{N}_3$  and  $\alpha$ -alkyn functionalized PgBiB-pSt. Further evidence of this coupling reaction was found from  $^1\text{H-}^1\text{H}$  COSY spectroscopic analysis. GPC analysis shows a clear molecular weight shift as a result of formation of the block copolymer.

**Acknowledgement.** This work was supported for two years by Pusan National University Research grant. The authors thank Son Kwang Jae (PNU Central Laboratory) for assistance with  $^1\text{H-}^1\text{H}$  NMR COSY Spectroscopic analysis.

## References

- (1) N. Hadjichristidis, S. Pispas, and G. Floudas, *Block Copolymers*, Wiley, Hoboken, NJ, 2003.
- (2) K. Matyjaszewski and T. P. Davis, Eds., *Handbook of Radical Polymerization*, Wiley, Hoboken, NJ, 2002.
- (3) J. S. Wang and K. Matyjaszewski, *J. Am. Chem. Soc.*, **117**, 5614 (1995).
- (4) K. Matyjaszewski and J. Xia, *Chem. Rev.*, **101**, 2921 (2001).
- (5) M. Kamigaito, T. Ando, and M. Sawamoto, *Chem. Rev.*, **101**, 3689 (2001).
- (6) Y.-J. Kwark, J. Kim, and B. M. Novak, *Macromol. Res.*, **15**, 31 (2007).
- (7) H. Y. Cho, B. H. Han, I. Kim, and H.-j. Paik, *Macromol. Res.*, **14**, 539 (2006).
- (8) S. C. Hong, W. S. Lyoo, K. E. Shin, and S. K. Noh, *Macromol. Res.*, **13**, 391 (2005).
- (9) M. Kang and B. Moon, *Macromol. Res.*, **13**, 229 (2005).
- (10) Y. W. Lee, S. M. Kang, K. R. Woon, Y. S. Chi, I. S. Choi, S. P. Hong, B. C. Yu, H.-j. Paik, and W. S. Yun, *Macromol. Res.*, **13**, 356 (2005).
- (11) V. Coessens, T. Pintauer, and K. Matyjaszewski, *Prog. Polym. Sci.*, **26**, 337 (2001).
- (12) V. Coessens and K. Matyjaszewski, *J. Macromol. Sci. Pure Appl. Chem. A*, **36**, 667 (1999).
- (13) S. G. Gaynor, Y. Nakagawa, and K. Matyjaszewski, *Macromol. Rapid Comm.*, **18**, 1057 (1997).
- (14) R. Huisgen, *Angew. Chem. Int. Ed.*, **2**, 565 (1963).
- (15) V. V. Rostovtsev, L. G. Green, V. V. Fokin, and K. B. Sharpless, *Angew. Chem. Int. Ed.*, **41**, 2596 (2002).
- (16) C. W. Tornøe, C. Christensen, and M. Meldal, *J. Org. Chem.*, **67**, 3057 (2002).
- (17) H. Li, F. Cheng, A. M. Duft, and A. Adronov, *J. Am. Chem. Soc.*, **127**, 14518 (2005).

- (18) B. S. Sumerlin, N. V. Tsarevsky, G. Louche, R. Y. Lee, and K. Matyjaszewski, *Macromolecules*, **38**, 7540 (2005).
- (19) B. S. Sumerlin, N. V. Tsarevsky, H. Gao, P. Golas, G. Louche, R. Y. Lee, and K. Matyjaszewski, *ACS Sym. Ser.*, **944**, 140 (2006).
- (20) H. Gao, G. Louche, B. S. Sumerlin, N. Jahed, P. Golas, and K. Matyjaszewski, *Macromolecules*, **38**, 8979 (2005).
- (21) P. Wu, A. K. Feldman, A. Nugent, K. Hawker, C. J. Scheel, A. Voit, B. Pyun, J. Frechet, K. B. Sharpless, and V. V. Fokin, *Angew. Chem. Int. Ed.*, **43**, 3928 (2004).
- (22) M. J. Joralemon, R. K. O'Reilly, J. B. Matson, A. K. Nugent, C. J. Hawker, and K. L. Wooley, *Macromolecules*, **38**, 5436 (2005).
- (23) E. Fernandez-Megia, J. Correa, I. Rodriguez-Meizoso, and R. Riguera, *Macromolecules*, **39**, 2113 (2006).
- (24) M. J. Joralemon, R. K. O'Reilly, C. J. Hawker, and K. L. Wooley, *J. Am. Chem. Soc.*, **127**, 16892 (2005).
- (25) H. Gao and K. Matyjaszewski, *Macromolecules*, **39**, 4960 (2006).
- (26) B. A. Laurent and S. M. Grayson, *J. Am. Chem. Soc.*, **128**, 4238 (2006).
- (27) J. A. Opsteen and J. C. M. van Hest, *Chem. Comm.*, **57**, (2005).
- (28) H. Durmaz, B. Colakoglu, U. Tanka, and G. Hizal, *J. Polym. Sci.; Part A: Polym. Chem.*, **44**, 1667 (2006).
- (29) D. Quemener, T. P. Davis, C. Barner-Kowollik, and M. H. Stenzel, *Chem. Comm.*, 5051 (2006).
- (30) K. Matyjaszewski, T. E. Patten, and J. Xia, *J. Am. Chem. Soc.*, **119**, 674 (1997).
- (31) A. E. Luedtke and J. W. Timberlake, *J. Org. Chem.*, **50**, 268 (1985).
- (32) N. V. Tsarevsky, B. S. Sumerlin, and K. Matyjaszewski, *Macromolecules*, **38**, 3558 (2005).
- (33) H.-j. Paik, S. Gaynor, and K. Matyjaszewski, *Macromol. Rapid Comm.*, **19**, 47 (1998).
- (34) J. F. Lutz, H. G. Boerner, and K. Weichenhan, *Macromol. Rapid Comm.*, **26**, 514 (2005).
- (35) J. F. Lutz, H. G. Boerner, and K. Weichenhan, *Macromolecules*, **39**, 6376 (2006).
- (36) J. F. Lutz and K. Matyjaszewski, *Macromol. Chem. Phys.*, **203**, 1385 (2002).
- (37) J. F. Lutz and K. Matyjaszewski, *J. Polym. Sci.; Part A: Polym. Chem.*, **43**, 897 (2005).
- (38) P. V. Andrew and S. S. Brent, *Macromolecules*, **39**, 5286 (2006).