



## Synthesis of poly[methyl(3,3,3-trifluoropropyl)siloxane]- *b*-poly(ethylene oxide) block copolymers\*

Xiao-li ZHAN<sup>1</sup>, Bi CHEN<sup>1</sup>, Qing-hua ZHANG<sup>†‡1</sup>, Ling-min YI<sup>2</sup>, Bo JIANG<sup>1</sup>, Feng-qiu CHEN<sup>1</sup>

(<sup>1</sup>College of Materials Science and Chemical Engineering, Zhejiang University, Hangzhou 310027, China)

(<sup>2</sup>MOE Key Laboratory of Advanced Textile Materials and Manufacturing Technology, Zhejiang Sci-Tech University,  
Hangzhou 310018, China)

<sup>†</sup>E-mail: qhzhang@zju.edu.cn

Received May 3, 2008; revision accepted June 13, 2008

**Abstract:** A series of new amphiphilic poly[methyl(3,3,3-trifluoropropyl)siloxane]-*b*-poly(ethylene oxide) (PMTFPS-*b*-PEO) diblock copolymers with different ratios of hydrophobic segment to hydrophilic segment were prepared by coupling reactions of end-functional PMTFPS and PEO homopolymers. Copolymers were shown to be well defined and narrow molecular weight distribution (MWD) (1.07~1.3) by characterizations such as gel permeation chromatography (GPC) and <sup>1</sup>H-nuclear magnetic resonance (<sup>1</sup>H-NMR).

**Key words:** Block copolymers, Polysiloxanes, Fluoropolymers, Synthesis, Polyethyleneoxide

**doi:** 10.1631/jzus.A0820162

**Document code:** A

**CLC number:** TQ31; O63

### INTRODUCTION

Polysiloxane-based copolymers, as we know, exhibit unique properties such as high hydrophobicity and flexibility, optical transparency, biocompatibility, etc. These characteristics make polysiloxanes interesting as blocks for the preparation of amphiphilic copolymers with properties different from those of many other purely organic polymers. A special example of amphiphilic copolymers based on polysiloxane is the so-called “superspreaders” consisting of trisiloxanes and polyethers (Rosen and Wu, 2001; Wu and Rosen, 2002). The remarkable surface-active properties of the “superspreaders” have received much attention. Several researchers (Lin *et al.*, 1994; Kickelbick *et al.*, 2003a; 2003b) also carried out detailed investigation into the solution properties of copolymers comprising polysiloxane and polyether. Their potential to aggregate in aqueous solutions was

shown by these studies and spontaneous vesicle formations were reported for amphiphilic block copolymers comprising poly(dimethylsiloxane) and poly(ethylene oxide) (PEO). On the other hand, polymers containing fluorinated alkyl side chains have also attracted great attention due to their amazing properties (Zhang *et al.*, 2007), such as high chemical and thermal stability, outstanding anti-adhesive and oil-repellent properties, low refractive index and low dielectric constant. Incorporation of fluorinated alkyl group into the polysiloxane chain will result in polysiloxane with many properties even superior to poly(dimethylsiloxane). Hence, better performances can be anticipated for amphiphilic copolymers based on fluorinated polysiloxane instead of poly-(dimethylsiloxane). Higher incompatibility between hydrophobic and hydrophilic segments will also bring about differences in solution behaviors and is worthy of investigation.

However, fluorinated polysiloxane-based amphiphilic copolymers were rarely reported. This may be caused by the difficulty of achieving narrow molecular weight distribution (MWD) fluorinated poly-

<sup>‡</sup> Corresponding author

\* Project supported by the National Natural Science Foundation of China (No. 20606029) and the Postdoctoral Science Foundation of China (No. 20070420230)

siloxanes. Severe “back-biting” and redistribution side reactions take place in the ring-opening polymerization (ROP) of fluoro-containing cyclosiloxane, resulting in very limited poly(fluorinated) siloxane homopolymers (10%~20%) with broad MWD when equilibrated (Yi *et al.*, 2005).

In our work, a series of amphiphilic diblock copolymers comprising poly[methyl(3,3,3-trifluoropropyl)siloxane] (PMTFPS) and PEO with a different ratio of the hydrophobic segment to the hydrophilic segment were prepared. The MWDs of PMTFPS-*b*-PEO diblock copolymers synthesized were controlled between 1.07 to 1.30 by careful selection of polymerization and purification methods.

## EXPERIMENT

### Materials

1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)cyclotrisiloxane (F<sub>3</sub>) (99.9%, Shanghai 3F Co.) was first dried over 3 Å molecular sieves, then refluxed in CaH<sub>2</sub> for 2 h and finally vacuum distilled into ampoules. *n*-butyllithium (BuLi) in hexane (2 mol/L) was purchased from Aldrich and titrated before use (Gilman and Cartledge, 1964). Tetrahydrofuran (THF) (99%, Sinopharm Chemical Reagent Co.) was refluxed in sodium until it turned blue with the addition of diphenyl ketone. Dimethylchlorosilane (98%) was purchased from Aldrich and distilled before use. Speier's catalyst was prepared dissolving H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (Sinopharm Chemical Reagent Co., AR) in isopropanol to form 0.01 mol/L solution. Toluene (99.5%, Sinopharm Chemical Reagent Co.) was distilled from sodium. Methanol (99%, Sinopharm Chemical Reagent Co.) was used as precipitator. Allyl terminated PEO was kindly provided by Clariant Corporation and characterized by gel permeation chromatography (GPC) (*MWD*<1.2) before use. Other solvents used in the experiments were purified according to standard methods.

### Synthesis of Si-H functional PMTFPS homopolymers

A high vacuum technique was used to maintain a “pure” reaction environment (10<sup>-3</sup> Pa) before Ar was filled to protect the reaction system. *n*-BuLi was first transferred to the reactor under the protection of Ar.

F<sub>3</sub> was dissolved in THF to form a clear solution and subsequently the solution was added into the reactor to start the reaction. The addition of the THF solution of F<sub>3</sub> was divided into two steps: (1) a certain amount of solution was added (1.2 mol F<sub>3</sub>/mol *n*-BuLi) and stirred for 1 h at 0 °C; (2) the residual solution was added and stirred for another 2 h at 0 °C. In both steps, monomer concentration was kept above 1.3 mol/L to yield narrow MWD homopolymers according to our previous work (Yi *et al.*, 2005). Dimethylchlorosilane was added to terminate the reaction and the solution was stirred for another 12 h at room temperature. The resultant mixture was centrifuged for 10 min and separated. The organic phase was vacuum distilled to remove remained solvent.

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, δ): 0~0.22 [m, OSi(CH<sub>3</sub>)<sub>2</sub>O], 0.58~0.65 [t, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si], 0.70~0.81 [t, CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Si], 0.85~0.95 [t, CH<sub>3</sub>CH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>Si], 1.25~1.40 [m, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si], 1.90~2.15 [t, CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Si], 4.73~4.75 [s, SiH].

### Preparation of PMTFPS-*b*-PEO block copolymers

A 50% (w/w) toluene solution of Si-H terminated PMTFPS homopolymer and allyl terminated PEO homopolymer (1.2 mol/mol Si-H groups) was stirred aggressively at room temperature in nitrogen atmosphere. The polymers were coupled by hydrosilation reaction applying 10<sup>-4</sup> mol/mol double bond Speier's catalyst. The solution was heated to 80 °C and stirred for 24 h. After the completion of the hydrosilation reaction, the solvent was vacuum distilled. Products were purified using methanol as the precipitator.

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, δ): 0~0.22 [m, OSi(CH<sub>3</sub>)<sub>2</sub>O], 0.58~0.65 [t, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si], 0.70~0.81 [t, CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Si], 0.85~0.95 [t, CH<sub>3</sub>CH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>Si], 1.25~1.40 [m, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si], 1.90~2.15 [t, CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Si], 3.38~3.42 [CH<sub>3</sub>O-(CH<sub>2</sub>)<sub>2</sub>O], 3.50~3.80 [O(CH<sub>2</sub>)<sub>2</sub>O].

### Characterization methods

GPC analysis was performed on a Waters 1525/2414 GPC system consisting of a Waters 1525 binary high-performance liquid chromatography pump, a Waters 717 plus autosampler, three Waters Styragel columns (Styragel HR2, HR3 and HR4) and a Waters 2414 refractive-index detector, and THF was used as eluent at a flow rate of 1.0 ml/min at 40 °C.

The calibration curve was made with polystyrene (PS) standards (Waters Co.). For PEO homopolymers the molecular weights calculated with the PS calibration were transformed into PEO molecular weights via "universal calibration" (Grubisic *et al.*, 1996). Mark-Houwink constants used for "universal calibration" were:  $K_{PS}=0.0288$ ,  $\alpha_{PS}=0.61$ ,  $K_{PEO}=0.0135$  and  $\alpha_{PEO}=0.78$ , where the subscript correspond to respective homopolymers (Robert *et al.*, 1997).

$^1\text{H-NMR}$  analysis was conducted with a Bruker 500 MHz nuclear magnetic resonance spectrometer (Advance DMX500) and was carried out with a 5% (w/w) solution in  $\text{CDCl}_3$  at room temperature.

Infrared spectra of the polymers were recorded on a Nicolet 5700 Fourier transform infrared (FT-IR) instrument. The polymer films were cast onto KBr disks to be analyzed.

## RESULTS AND DISCUSSION

Si-H functional PMTFPS homopolymers were prepared via anionic ROP of  $\text{F}_3$  terminated with dimethylchlorosilane. Applying Speier's catalyst to a solution of purified Si-H functional PMTFPS and allyl terminated PEO homopolymers, a variety of amphiphilic copolymers consisting of PMTFPS and PEO with different block lengths were synthesized (Fig.1).

As we know, the control of the MWD of each block is critical for the preparation of block copolymers with narrow MWD. However, for many ROP processes, if monomer conversion is greater than 85%, backbiting reactions were no longer neglectable (Elkins and Long, 2004). In order to minimize backbiting reactions and achieve narrow distributed PMTFPS homopolymers, conversions of our reactions were limited to 80%. The influence of polymerization

conditions on the homopolymer has been carefully studied in our previous work using poly(styrene lithium) (PSLi) as initiator (Yi *et al.*, 2005). High monomer concentration was shown to effectively inhibit backbiting and redistribution side reactions. The monomer concentration for our anionic ROPs was kept above 1.3 mol/L. The purity of PMTFPS homopolymers was proved by GPC analysis. No monomer residues were detected after the purification procedure in these homopolymers.

The coupling reaction between purified Si-H functional PMTFPS and allyl terminated PEO homopolymers was followed and the comparison of  $^1\text{H-NMR}$  spectra of PMTFPS homopolymer and PMTFPS-*b*-PEO diblock copolymer was shown in Fig.2. As can be seen, Si-H group resonance located around  $\delta$  4.7 disappeared completely after the coupling reaction which suggested the completeness of the hydrosilation reaction. And also, the peaks located around  $\delta$  0.6 assigned to the methylene group bonded to silicon nearly doubled after the coupling reaction, which showed another support for the successful preparation of PMTFPS-*b*-PEO diblock copolymers. Newly formed peaks corresponded to hydrogen on the PEO chain. Properties of amphiphilic PMTFPS-*b*-PEO diblock copolymers are summarized in Table 1. PMTFPS-*b*-PEO diblock copolymers with MWDs ranging from 1.07 to 1.30 were successfully synthesized.

Note that  $M_n$  values calculated by GPC characterization are not absolute values. As can be seen from Table 1, there are discrepancies between the  $M_n$  values determined by  $^1\text{H-NMR}$  and  $M_n$  values determined by GPC concerning PMTFPS homopolymers. The reason is attributed to the fact that the  $M_n$  values determined by GPC are relative values calibrated with linear PS standards.

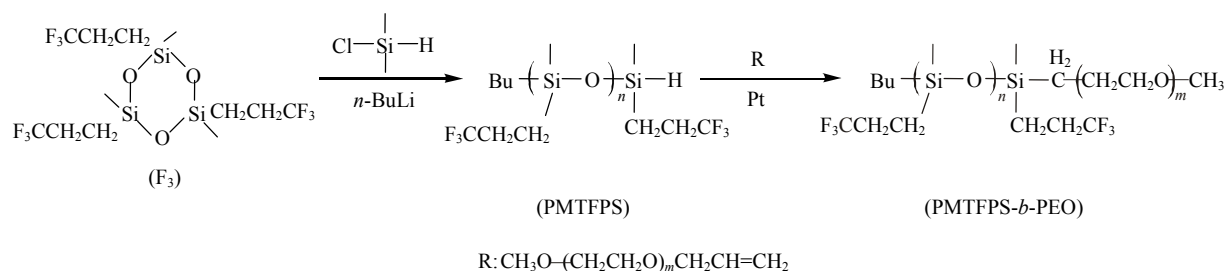


Fig.1 Synthesis of PMTFPS-*b*-PEO diblock copolymers

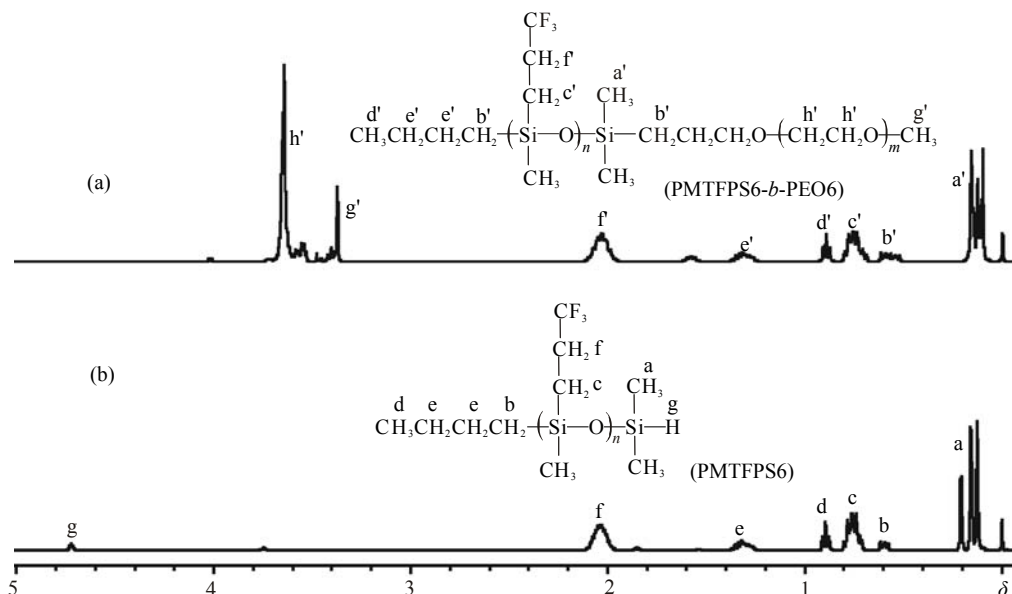


Fig.2 Comparison of <sup>1</sup>H-NMR spectra of Si-H functional (a) PMTFPS-*b*-PEO diblock copolymer and (b) PMTFPS homopolymer

Table 1 Properties of prepared PMTFPS-*b*-PEO diblock copolymers

Sample	PMTFPS		Diblock	PEO
	$M_n^a$	$M_n^b (M_w/M_n)^b$	$M_n^b (M_w/M_n)^b$	$M_n^c$
PMTFPS6- <i>b</i> -PEO6	1114	1417 (1.11)	1770 (1.15)	350
PMTFPS6- <i>b</i> -PEO9	1114	1417 (1.11)	2239 (1.16)	450
PMTFPS6- <i>b</i> -PEO23	1114	1417 (1.11)	2579 (1.18)	1100
PMTFPS9- <i>b</i> -PEO6	1738	2092 (1.15)	2363 (1.30)	350
PMTFPS9- <i>b</i> -PEO9	1738	2092 (1.15)	2751 (1.10)	450
PMTFPS9- <i>b</i> -PEO23	1738	2092 (1.15)	3518 (1.07)	1100

<sup>a</sup>Determined by <sup>1</sup>H-NMR in CDCl<sub>3</sub> using the resonances of trifluoropropyl groups between  $\delta$  1.9 and  $\delta$  2.15 in comparison to the methylene group bonded to silicon found between  $\delta$  0.58 and  $\delta$  0.65; <sup>b</sup>Determined by GPC with PS calibration; <sup>c</sup>Determined by GPC, based on PS calibration and calculated into PEO molecular weight

## CONCLUSION

In summary we showed that amphiphilic block copolymers consisting of a PMTFPS hydrophobic block and a PEO hydrophilic block could be easily synthesized by coupling reactions of two separate end-functionalized segments. The MWDs of these PMTFPS-*b*-PEO diblock copolymers range from 1.07 to 1.3. And we are still exploring the possible application of these new amphiphilic block copolymers. Self-assembly behavior of the synthesized block copolymers is being investigated by our research group and we would like to report when substantial progress is made.

## References

- Elkins, C.L., Long, T.E., 2004. Living anionic polymerization of hexamethylcyclotrisiloxane (D3) using functionalized initiation. *Macromolecules*, **37**(17):6657-6659. [doi:10.1021/ma049188n]
- Gilman, H., Cartledge, F., 1964. The analysis of organolithium compounds. *Journal of Organometallic Chemistry*, **2**(6): 447-454. [doi:10.1016/S0022-328X(00)83259-3]
- Grubisic, Z., Rempp, P., Benoit, H., 1996. A universal calibration for gel permeation chromatography. *Journal of Polymer Science Part B: Polymer Physics*, **34**(10):1707-1713. [doi:10.1002/polb.1996.922]
- Kickelbick, G., Bauer, J., Huesing, N., Andersson, M., Palmqvist, A., 2003a. Spontaneous vesicle formation of short-chain amphiphilic polysiloxane-*b*-poly(ethylene oxide) block copolymers. *Langmuir*, **19**(8):3198-3210.

- [doi:10.1021/la026763c]
- Kickelbick, G., Bauer, J., Huesing, N., Andersson, M., Holmberg, K.A., 2003b. Aggregation behavior of short-chain PDMS-*b*-PEO diblock copolymers in aqueous solutions. *Langmuir*, **19**(24):10073-10076. [doi:10.1021/la035063k]
- Lin, Z., Hill, R.M., Davis, H.T., Scriven, L.E., Talmon, Y., 1994. Cryo transmission electron microscopy study of vesicles and micelles in siloxane surfactant aqueous solutions. *Langmuir*, **10**(4):1008-1011. [doi:10.1021/la00016a009]
- Robert, E., Fighter, J., Godin, N., Boscher, Y., 1997. Discussion on round-robin testing in size exclusion chromatography using polyamides as an example. *International Journal of Polymer Analysis and Characterization*, **3**(4):351-358.
- Rosen, M.J., Wu, Y., 2001. Superspreading of trisiloxane surfactant mixtures on hydrophobic surfaces. 1. Interfacial adsorption of aqueous trisiloxane surfactant-*N*-alkyl pyrrolidinone mixtures on polyethylene. *Langmuir*, **17**(23):7296-7305. [doi:10.1021/la010466a]
- Wu, Y., Rosen, M.J., 2002. Superspreading of trisiloxane surfactant mixtures on hydrophobic surfaces. 2. Interaction and spreading of aqueous trisiloxane surfactant-*N*-alkyl-pyrrolidinone mixtures in contact with polyethylene. *Langmuir*, **18**(6):2205-2215. [doi:10.1021/la0113318]
- Yi, L., Zhan, X., Chen, F., Du, F., Huang, L., 2005. Synthesis and characterization of poly[styrene-*b*-methyl(3,3,3-trifluoropropyl)siloxane] diblock copolymers via anionic polymerization. *Journal of Polymer Science Part A: Polymer Chemistry*, **43**(19):4431-4438. [doi:10.1002/pola.20927]
- Zhang, Q.H., Zhan, X.L., Chen, F.Q., Shi, Y., Wang, Q.Y., 2007. Block copolymers of dodecafluoroheptyl methacrylate and Butyl methacrylate by RAFT miniemulsion polymerization. *Journal of Polymer Science Part A: Polymer Chemistry*, **45**(9):1585-1594. [doi:10.1002/pola.21930]