

Supplementary Information

Well-defined polyethylene-based graft terpolymers by combining nitroxide-mediated radical polymerization, polyhomologation and azide/alkyne “click” chemistry†

Nazeeha Alkayal,^a Hakan Durmaz,^b Umit Tunca,^{b*} Nikos Hadjichristidis^{a*}

^aKing Abdullah University of Science and Technology (KAUST), Physical Sciences and Engineering Division, KAUST Catalysis Center, Polymer Synthesis Laboratory, Thuwal 23955, Saudi Arabia

^bDepartment of Chemistry, Istanbul Technical University, Maslak 34469, Istanbul, Turkey.

Experimental details

Synthesis of dimethylsulfoxonium methylide¹

In a three-necked flask connected to a condenser and an argon/vacuum line, 6.8 g of NaH (dispersed in mineral oil, 60% in weight) was introduced and washed with dry petroleum ether (20 mL×3). The residual solvent was removed under vacuum, followed by the addition of 20 g of dry trimethylsulfoxonium chloride and 200 mL of THF. The entire operation was performed under argon flow. The mixture was heated and refluxed at 70°C until cessation of the gas (4-5 h). After the reaction, the THF was removed under low pressure and 50 mL of dry toluene was added. The solution was filtered through a dry celite-545 column (2-3 cm). The flask and filtration cake were washed with 200 mL fresh toluene. A clear solution with a light yellow color was obtained, which was titrated with a standard HCl aqueous solution (0.73 mmol/mL).

Synthesis of Merrifield’s resin-azide²

Merrifield’s resin (1 g, 1 mmol) was suspended in DMF (30 mL), and (2.6 g, 40 mmol) sodium azide was added to the mixture. The reaction mixture was stirred overnight at 80 °C, then filtered, washed with distilled water, methanol, and acetone to give Merrifield’s resin with methyl-azido functionalities and dried in vacuum oven at 25 °C.

General procedure for the treatment of graft terpolymers with Merrifield’s resin-azide to remove the unreacted PE-*b*-PCL-alkyne copolymer ²

The crude graft terpolymers PSt-*g*-(PCL-*b*-PE) were dissolved in toluene in a Schlenk tube. 20 eq. of CuBr and PMDETA were added to the solution followed by addition of 0.1 g of Merrifield’s resin-azide. The mixture was degassed by three freeze-pump-thaw (FTP) cycles and stirred under argon at 80 °C for 2 days. The obtained polymers were passed through a neutral alumina column to remove the copper and then precipitated in methanol and dried under vacuum at room temperature.

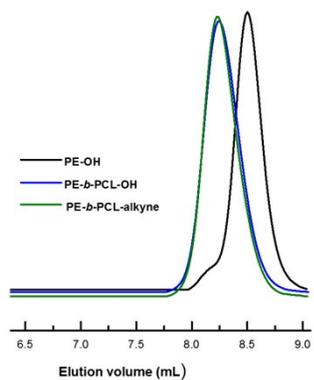


Figure S1. HT-SEC chromatograms of PE-OH, PE-*b*-PCL-OH and PE-*b*-PCL-alkyne in 1,2,4-trichlorobenzene at 150 °C.

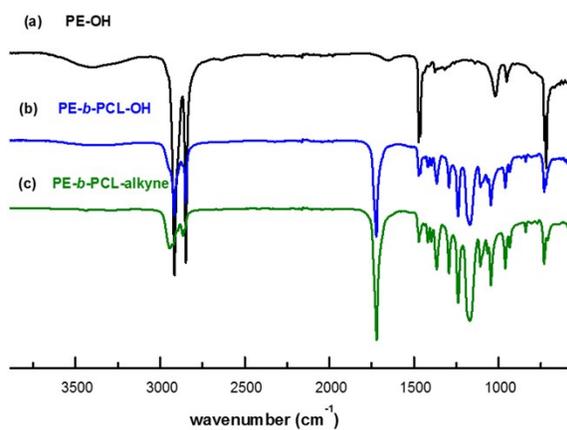


Figure S2. IR spectra of PE –OH, PE-*b*-PCL-OH and PE-*b*-PCL-alkyne.

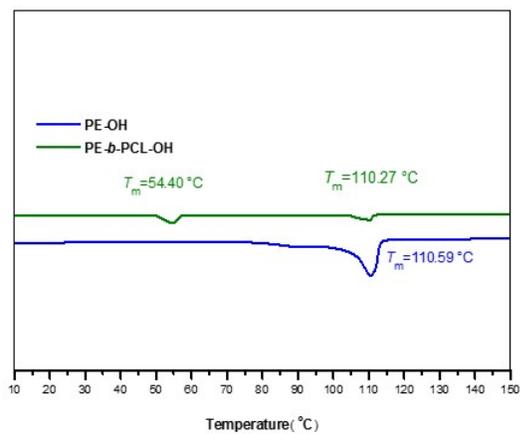


Figure S3. DSC traces of PE–OH and PE-*b*-PCL-OH (N₂ atmosphere, 10 °C/ min, second heating cycle).

Copolymerization of St and 4-CMS to synthesize poly (styrene-*co*-chloro methyl styrene), poly(St-*co*-4-CMS), under NMP conditions

Poly(St-*co*-4-CMS) was prepared *via* NMP of styrene and 4-CMS at 125°C. In a 50 mL of Schleck tube, St (5.0 mL, 0.047 mmol), 4-CMS (2.84 mL, 0.200 mmol), TEMPO (0.127 g, 0.8 mmol), BPO (0.151 g, 0.620 mmol) were added, the reaction mixture was degassed by three FPT cycles. The tube was placed in a thermostatic oil bath at 125°C for 17 h, the polymerization mixture was precipitated in methanol and dried for 24 h in vacuum oven at 30°C (2.5 g, 32 % yield, $M_{n, NMR} = 9950 \text{ g}\cdot\text{mol}^{-1}$). The random copolymer contains 25 CMS units, as determined by ^1H NMR in CDCl_3 (Figure S4), and is labeled as poly (St-*co*-4-CMS)-25 in this text. Another copolymerization was carried out using the following monomers and initiator feed: St (5 mL, 0.047 mmol), CMS (6.6 mL, 0.047 mmol), TEMPO (0.22 g, 0.940 mmol) and BPO (0.19 g, 0.940 mmol) under same conditions. The copolymer was precipitated in methanol and dried for 24 h in vacuum oven at 30 °C (5.0 g, 43 % yield, $M_{n, NMR} = 15400 \text{ g}\cdot\text{mol}^{-1}$). This copolymer contains 55 4-CMS units, as analyzed by ^1H NMR (Figure S4), and is labeled poly(St-*co*-4-CMS)-55. A typical ^1H NMR spectrum of the copolymers (Figure S4) (600 MHz, CDCl_3) shows the following peaks: 6.5-7.5 ppm (m, 9H, ArH of PSt and P (4-CMS)), 4.5 ppm (s, 2H, Ph- $\text{CH}_2\text{-Cl}$, P (4-CMS)), 2.2-0.6 ppm (m, 2H, aliphatic protons).

Synthesis of poly (styrene-*co*-azido methyl styrene), (poly (St-*co*-4-AMS)

1 g of poly (St-*co*-4-CMS)-25 or 1.5 g poly (St-*co*-4-CMS)-55 was dissolved in DMF (15 mL), followed by addition of sodium azide (0.61 g, 9.400 mmol). The mixture was stirred at room temperature overnight. The obtained polymers poly(St-*co*-4-AMS) were precipitated in methanol and dried in vacuum oven at 25 °C. The following results were obtained: poly(St-*co*-4-AMS)-25 (0.95 g, 95 % yield, $M_{n, NMR} = 10200 \text{ g}\cdot\text{mol}^{-1}$) and poly(St-*co*-4-AMS)-55 (1.2 g, 80 % yield, $M_{n, NMR} = 15800 \text{ g}\cdot\text{mol}^{-1}$) in this work. A typical ^1H NMR spectrum (Figure S4) (600 MHz, CDCl_3) includes the following peaks: 6.5-7.5 ppm (m, 9H, ArH of PSt and P (4-CMS)), 4.23ppm (s, 2H, Ph- $\text{CH}_2\text{-N}_3$, P (4-CMS)), and 2.2-0.6 ppm (m, 2H, aliphatic protons).

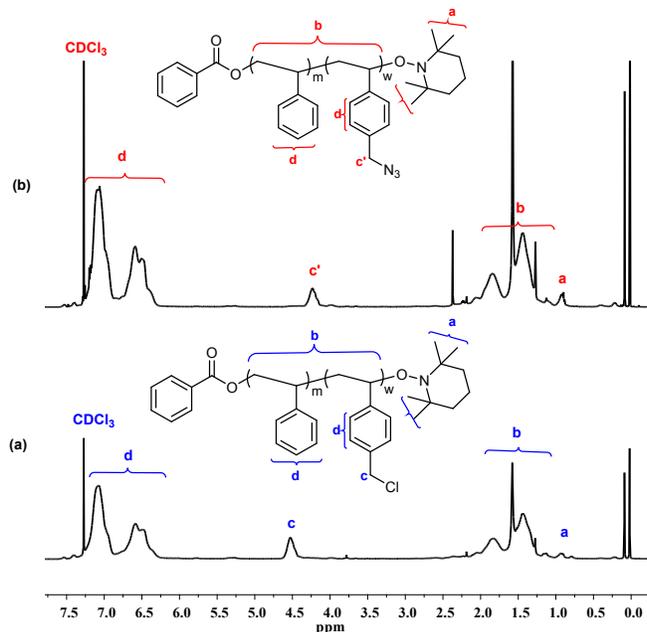


Figure S4 ^1H NMR spectra (a) poly (St-co-4-CMS) and (b) poly (St-co-4-AMS) in CDCl_3 (600 MHz).

Results and discussion on the synthesis of poly(St-co-4-CMS) and poly(St-co-4-AMS)

Table S1 Molecular weights of the backbone polymers at various stages

No.	Feed ratio St/CMS ^a	Poly (St-co-4-CMS)			Poly (St-co-4-AMS)		
		$M_{n, \text{SEC}}^b$ ($\text{g}\cdot\text{mol}^{-1}$)	PDI^b	$M_{n, \text{NMR}}^c$ ($\text{g}\cdot\text{mol}^{-1}$)	$M_{n, \text{SEC}}^b$ ($\text{g}\cdot\text{mol}^{-1}$)	PDI^b	$M_{n, \text{NMR}}^c$ ($\text{g}\cdot\text{mol}^{-1}$)
1	65/35	10600	1.15	9950	11600	1.13	10200
2	47/53	15900	1.32	15400	17900	1.29	15800

^a Feed ratio of St and 4-CMS = $M_{n, \text{SEC}} \times (\text{composite of CMS or AMS were calculated from the ratio of the signal at 4.50 or 4.22 ppm to the total area between 6.30-7.50 ppm}) / M_w$ of CMS. ^b SEC in THF as the eluent and PST-based calibration. ^c $M_{n, \text{NMR}}$ of copolymers were calculated from the ratio of integrated values of signal at 0.9 ppm to the signals at 4.50 or 4.22 ppm and signal at 6.50 ppm.

The SEC-THF traces in Figure S5 showing the monomodal distribution demonstrated the successful transformation of chlorides to azide groups and indicated that was no change of apparent molecular weight between poly (St-co-4-CMS) and poly (St-co-4-AMS). According to Scheme 2, the pendent chlorides of poly (St-co-4-CMS) can be converted into azide groups by reaction with the excess of NaN_3 in DMF overnight at room temperature to yield poly (St-co-4-AMS). ^1H NMR proves that the substitution of the pendent chloride groups into azide groups is quantitative. The typical FTIR spectra of the starting

copolymer and the product after reaction with NaN_3 are presented in Figure S6. A strong absorbance peak was observed at 2104 cm^{-1} related to the azide group.

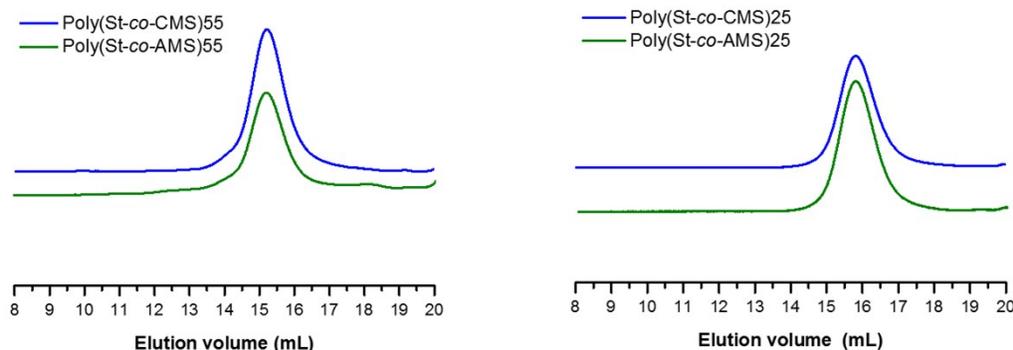


Figure S5. SEC-THF traces of (a) poly(St-co-4-CMS)-25, poly(St-co-4-AMS)-25 and (b) poly(St-co-4-CMS)-55, poly(St-co-4-AMS)-55 in THF at $35\text{ }^\circ\text{C}$.

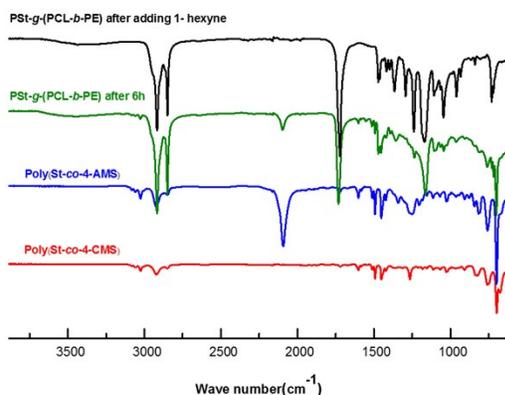


Figure S6. IR spectra of (a) poly(St-co-4-CMS), (b) poly(St-co-4-AMS), (c) PST-g-(PCL-b-PE) before and (d) after adding 1-hexyne.

References

1. B. B. Busch, M. M. Paz, K. J. Shea, C. L. Staiger, J. M. Stoddard, J. R. Walker, X.-Z. Zhou, H. Zhu, *J. Am. Chem. Soc.*, 2002, **124**, 3636–3646.
2. E. Gungor, H. Durmaz, G. Hizal, U. Tunca, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 4459-4468.