A Versatile Approach for the Preparation of End-Functional Polymers and Block Copolymers by Stable Radical Exchange Reactions†

Yonca Alkan Goksu, Gorkem Yilmaz, Yusuf Yagci
Department of Chemistry, Istanbul Technical University, Maslak 34469, Istanbul, Turkey
Correspondence to: Y. Yagci (E-mail: yusuf@itu.edu.tr)

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ABSTRACT: A versatile strategy for the preparation of end-functional polymers and block copolymers by radical exchange reactions is described. For this purpose, first polystyrene with 2,2,6,6-tetramethylpiperidine-1-oxyl end group (PS-TEMPO) is prepared by nitroxide-mediated radical polymerization (NMRP). In the subsequent step, these polymers are heated to 130 °C in the presence of independently prepared TEMPO derivatives bearing hydroxyl, azide and carboxylic acid functionalities, and polymers such as poly(ethylene glycol) (TEMPO-PEG) and poly(ε-caprolactone) (TEMPO-PCL). Due to the simultaneous radical generation and reversible termination of the polymer radical, TEMPO moiety on polystyrene is replaced to form the corresponding end-functional polymers and block copolymers. The intermediates and final polymers are characterized by ^{1}H NMR, UV, IR, and GPC measurements. © 2019 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2019**

KEYWORDS: block copolymer; nitroxide mediated radical polymerization; radical coupling; stable radical; telechelic polymer

INTRODUCTION Strategies for controlling macromolecular architecture have witnessed explosive growth in the recent years. Controlled living/radical polymerization (CRP) techniques are of great importance for the synthesis of well-defined polymers with a wide range of chemical functionalities.[1] Among the various CRP techniques; atom transfer radical polymerization (ATRP),[2,3] reversible addition fragmentation (RAFT),[4] and nitroxide-mediated radical polymerization (NMRP)[5,6] are the most common methods. Due to its intrinsic simplicity, NMRP technique has advantages such as requirement of only monomer and unimolecular initiator, avoidance of sulfur, and metal catalysts used in RAFT and ATRP techniques.[5] Polymerization via NMRP technique is achieved through a stable nitroxide radical that caps the propagating polymer chain reversibly. As a result, low radical concentration is obtained in the solution and the termination and transfer reactions are minimized. After pioneering work of Georges *et al.*[7] who used 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) for controlling styrene polymerization, significant progress has been achieved to demonstrate the ability of TEMPO to control polymerization of styrene and styrene derivatives[5,8] and for the production of different complex macromolecular architectures, such as block copolymers,[9] polymer brushes,[10–13] star-shaped polystyrenes,[14] and hyperbranched copolymers.[15]

Synthesis of block copolymers are of a special interest since intermediary properties reflected by the individual segments could be obtained. Block copolymers have specific applications in a wide range of areas such as drug delivery,[16,17] holography,[18] solar cells,[19] and stimuli responsive materials[20] and their uses in other multidisciplinary platforms are rapidly expanding. Owing to this broad range of uses, there is an increasing demand for the synthesis of block copolymers with well-defined architectures.[21] Sequential monomer addition, mechanistic transformation, and segment coupling approaches are the most common methods for the syntheses of well-defined block copolymers. In sequential monomer addition approach, after the first monomer is consumed, another monomer is added to the reaction medium, and obtained block copolymer is isolated by precipitation.[22] The major drawback of this approach is that it is limited to monomers, which can only polymerize with the same mechanism. In the mechanistic transformation approach, one of the segments is synthesized by one polymerization mode and the other segment(s) by another mode. When compared to single mode polymerization strategies, mechanistic transformation method has several advantages particularly for the fabrication of block copolymers composed of structurally different monomer segments.[23] Mechanistic transformation reactions can be categorized into two subgroups: (a) direct and (b) indirect transformation. In direct transformation approach, propagating active center is transferred directly to another one with different polarity. However, short lifetime of propagating sites

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†Dedicated to Prof. Takeshi Endo on the occasion of his 80th birthday.

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limits the copolymerization process. On the other hand, indirect transformation is more attractive since reactive functional group for the second polymerization is introduced at the chain ends of the first polymer either in the initiation or termination steps. There is an expanding research on the application of mechanistic transformation methodologies on controlled/living radical polymerization processes.[24] In the third approach, two different segments are coupled in order to form a block copolymer. Diels-Alder and copper-catalyzed azide-alkyne cycloaddition reactions (CuAAC) are the most common examples of segment coupling approach.[25,26] We also showed CuAAC click reactions for the synthesis of various macromolecules such as block[27,28] and graft[29] copolymers.

In the frame of our ongoing interest in the development of synthetic routes for the preparation of well-defined macromolecular architectures, herein, we report a simple and versatile methodology for the preparation of end-functional polymers and block copolymers by radical exchange reactions. For this purpose, first, polystyrene is prepared by conventional NMRP technique using TEMPO and benzoyl peroxide as initiator. Next this polymer is heated to 130 °C in the presence of a variety of TEMPO derivatives having different functional groups namely hydroxyl (TEMPO-OH), azide (TEMPO-N_3), and carboxylic acid (TEMPO-COOH). Due to the simultaneous radical generation and reversible termination of the polymer radical, TEMPO moiety is replaced with TEMPO-OH, TEMPO-N_3, and TEMPO-COOH. In the context of a model experiment, CuAAC reaction between thus obtained azido functionalized polymer and alkyne functional pyrene is performed. The possibility of the formation of block copolymers through the same methodology by using TEMPO-functional poly(ε-caprolacton) (TEMPO-PCL) and poly(ethylene glycol) (TEMPO-PEG) is also demonstrated.

EXPERIMENTAL

Materials

Styrene (99%, Aldrich, Misouri, USA) was passed through a basic alumina column to remove the inhibitor. ε-Caprolactone (97%, Aldrich) was vacuum-distilled over molecular sieves before use. Benzoyl peroxide (75%, Aldrich) was recrystallized from ethanol. 2,2,6,6-Tetramethylpiperidine 1-oxyl (TEMPO, 98%, Aldrich) was purified by sublimation. 4-Hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO-OH, 97%, Merck, Darmstadt, Germany), 1-pyrenemethanol (98%, Aldrich), 4-pentynoic acid (95%, Aldrich), *N,N′*-dicyclohexylcarbodiimide (DCC, 99%, Aldrich), 4-(dimethylamino)pyridine (DMAP, >99%, Aldrich), succinic anhydride (>99%, Aldrich), tin(II)-2-ethylhexanoate (>92%, Aldrich), PEG-OMe (M_n = 2000, Aldrich), *p*-toluenesulfonyl chloride (TsCl, 99%, Aldrich), sodium hydride (NaH, 60% dispersion in mineral oil, Aldrich), triethylamine (>98%, J.Barker), ammonium chloride (>99%, Merck), hydrochloric acid (37%, Aldrich), magnesium sulfate (anhydrous, >99.5%, Aldrich), and sodium sulfate (anhydrous, >99%, Aldrich) were used as received. Dichloromethane (DCM, 99%, Merck) was distilled over CaH_2. Toluene (99.5% Carlo Erba, Milan, Italy) was dried by sodium and benzophenone as indicator and stored over molecular sieves under N_2. Dimethyl formamide (DMF, >99.8%, Aldrich) were dried over $4A^0$ molecular sieves before use. Diethyl ether (>98%, Aldrich), ethyl acetate (99.8%, Aldrich), hexane (95%, Aldrich), and tetrahydrofuran (THF, >99%, Aldrich) were used as received. Methanol (MeOH, technical) was used for the precipitation of polymers without further purification.

Instrumentation

^{1}H-NMR and ^{13}C-NMR of the intermediates and final polymers were recorded at room temperature at 500 and 125 MHz, respectively, on an Agilent VNMRS 500 spectrometer. FTIR analyses were carried out on a Perkin Elmer FTIR Spectrum One B. GPC measurements were performed on a TOSOH EcoSEC GPC system equipped with an auto sampler system, a temperature controlled pump, a column oven, a RI detector, a purge and degasser unit, and TSKgel superhZ2000, 4.6 mm ID × 15 cm × 2 cm column. THF was used as an eluent at flow rate of 1.0 mL min^{-1} at 40 °C. RI detector was calibrated with polystyrene standards having narrow molecular-weight distributions. Data were analyzed using Eco-SEC Analysis software.

Synthesis of TEMPO Functional Polystyrene (PS-TEMPO)

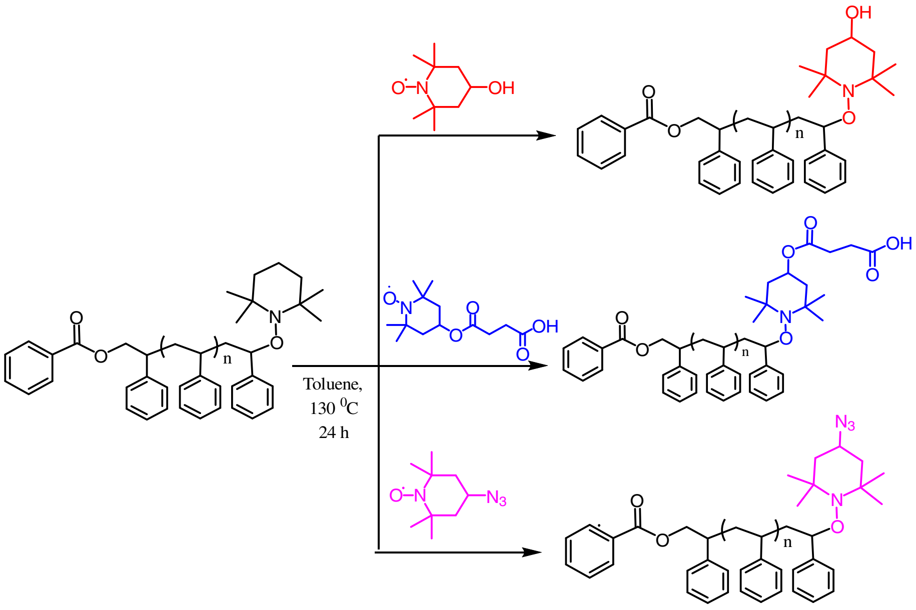
In a typical procedure, benzoyl peroxide (21 mg, 0,085 mmol), TEMPO (20 mg, 0,13 mmol), and styrene (2 ml, 17 mmol) in dry toluene (2 ml) were placed in a Schlenk tube equipped with stirring bar and Teflon stopcock. Reaction mixture was heated to 130 °C for 20 h. After termination of the reaction, the solution was in excess methanol and dried *in vacuo.* (Conv.: 28%, M_n = 1800, PDI = 1.11), ^{1}H NMR [500 MHz, $CDCl_3$, δ]: 7.20–6.50 (Ar), 5.74 (d, CH_2), 5.31 (t, CH), 1.83 (t, CH_2), 1.72 (m, CH_2), 1.27 (s, CH_3).

Synthesis of TEMPO-COOH

To a solution of TEMPO-OH (400 mg, 2.32 nm mmol) and DMAP (20 mg, 0.166 mmol) in anhydrous DCM (10 ml) cooled over ice-bath was added triethylamine (1.8 ml, 13 mmol). A solution of succinic anhydride (418 mg, 4.18 mmol) in anhydrous DCM (10 ml) was added dropwise. The solution was warmed up to room temperature and stirred overnight under nitrogen. Water (20 ml) and 10% HCl solution (6 ml) were added to reaction mixture. The aqueous layer was extracted with DCM twice. Combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give an orange oil. The oil was purified by silica gel column chromatography as 2:1 ethylacetate:hexane as mobile phase (R_f = 0.40). Product was obtained as orange solid. (54% yield). ^{1}H NMR [500 MHz, DMSO-d_6, $PhNHNH_2$, δ]: 5.01 (m, CH), 2.52 (t, CH_2), 2.49 (t, CH_2), 2.02 (dd, CH_2), 1.98 (dd, CH_2), 1.29 (s, CH_3), 1.26 (s, CH_3). FTIR (cm^{-1}): 2992, 1752, 1718, 1240, 1190.

Synthesis of TEMPO-OTs

To a solution of TEMPO-OH (0.4 g, 2.32 mmol) in 5 ml of pyridine, TsCl (0.57 g, 3 mmol) was added and it was stirred overnight at room temperature. The reaction mixture was diluted with chloroform, washed with 1 M HCl, saturated $NaHCO_3$ and brine, respectively. Organic phase was dried with $MgSO_4$, filtered and concentrated *in vacuo.* The residual was purified by column chromatography (silica gel) by using an



SCHEME 1 Synthesis of PS-TEMPO-OH, PS-TEMPO-COOH, and PS-TEMPO-N$_3$. [Color figure can be viewed at wileyonlinelibrary.com]

EtOAc/Petroleum spirit mixture (1:2, v/v) as mobile phase. The fraction at R$_f$ = 0.73 was collected and concentrated *in vacuo.* (187 mg, 25%). ^{1}H NMR [500 MHz, DMSO-d$_6$, PhNHNH$_2$, δ]: 8.50–7.42 (Ar), 4.71 (m, CH), 2.36 (s, CH$_3$), 1.64 (t, CH$_2$), 1.58 (t, CH$_2$), 1.28 (s, CH$_3$), 1.26 (s, CH$_3$). FTIR (cm^1): 1770, 1750, 1310, 1270.

Synthesis of TEMPO-N$_3$

To a solution of TEMPO-OTs (180 mg, 0.55 mmol) in DMF (5 mL), NaN$_3$ was added (71.5 mg, 1.1 mmol). Reaction was heated to 110 °C under N$_2$ overnight. Upon cooling, diethyl ether (30 ml) was added and mixture was washed with saturated NaHCO$_3$ solution and water, respectively. Organic phase was dried over MgSO$_4$ and concentrated *in vacuo.* Product was obtained as an orange solid (Yield: 30%). ^{1}H NMR [500 MHz, DMSO-d$_6$, PhNHNH$_2$, δ]: 3.60 (m, CH), 1.83 (t, CH$_2$), 1.57 (t, CH$_2$), 1.26 (s, CH$_3$), 1.23 (s, CH$_3$). FTIR (cm^{-1}): 2105 (N$_3$ stretching).

Synthesis of Hydroxyl Functional Polystyrene (PS-TEMPO-OH)

Previously flamed Schlenk tube equipped with a magnetic stirring bar was filled with PS-TEMPO (200 mg, 0.112 mmol) and TEMPO-OH (97 mg, 0.566 mmol) in 4 ml of dry toluene, and the mixture was stirred at 130 °C for 24 h. The resulting polymer was precipitated in methanol. (Conv: 84%, M_n = 2105, PDI = 1.09). ^{1}H NMR [500 MHz, CDCl$_3$, δ]: 6.25–7.23 (Ar), 5.74 (d, CH$_2$), 4.13 (t, CH), 2.51 (t, CH$_2$), 1.90 (m, CH$_2$), 1.52 (s, CH$_3$). FTIR (cm^{-1}): 3490 (-OH stretching).

Synthesis of Carboxylic Acid Functional Polystyrene (PS-TEMPO-COOH)

Previously flamed Schlenk tube equipped with a magnetic stirring bar was filled with PS-TEMPO (200 mg, 0.112 mmol) and TEMPO-COOH (154 mg, 0.566 mmol) in 4 ml of dry toluene and the mixture was stirred at 130 °C for 24 h. The resulting polymer was precipitated in methanol. (Conv: 85%, M_n = 2114, PDI = 1.095). ^{1}H NMR [500 MHz, CDCl$_3$, δ]: 6.26–7.23 (Ar), 5.74 (d, CH$_2$), 3.67 (t, CH), 2.58 (t, CH$_2$), 1.90 (m, CH$_2$), 1.52 (s, CH$_3$). FTIR (cm^{-1}): 2980, 1590, 1510, 1219, 1167.

Synthesis of Azido Functional Polystyrene (PS-TEMPO-N$_3$)

Previously flamed Schlenk tube equipped with a magnetic stirring bar was filled with PS-TEMPO (89 mg, 0.056 mmol) and TEMPO-N$_3$ (55 mg, 0.281 mmol) in 2 ml of dry toluene, and

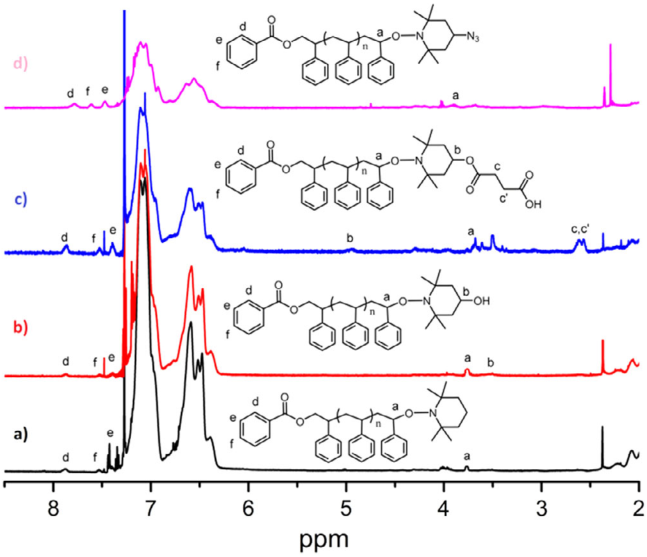


FIGURE 1 ^{1}H NMR spectra of (a) PS-TEMPO, (b) PS-TEMPO-OH, (c) PS-TEMPO-COOH, and (d) PS-TEMPO-N$_3$ [Color figure can be viewed at wileyonlinelibrary.com]

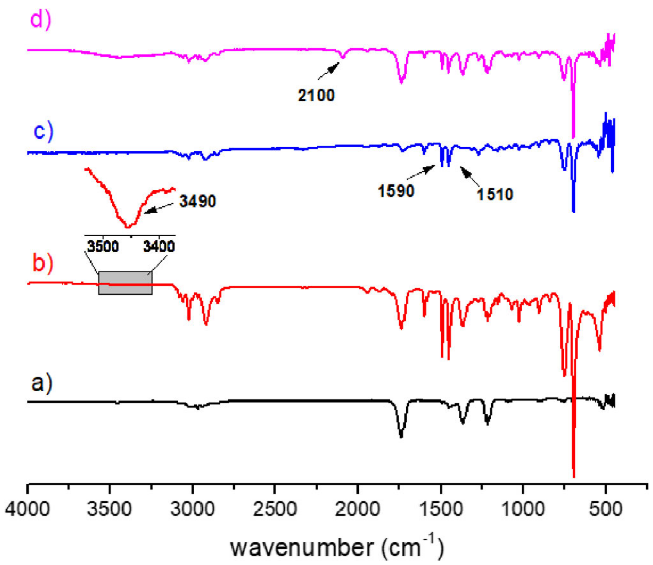


FIGURE 2 IR spectra of (a) PS-TEMPO, (b) PS-TEMPO-OH, (c) PS-TEMPO-COOH, and (d) PS-TEMPO-N_3 [Color figure can be viewed at wileyonlinelibrary.com]

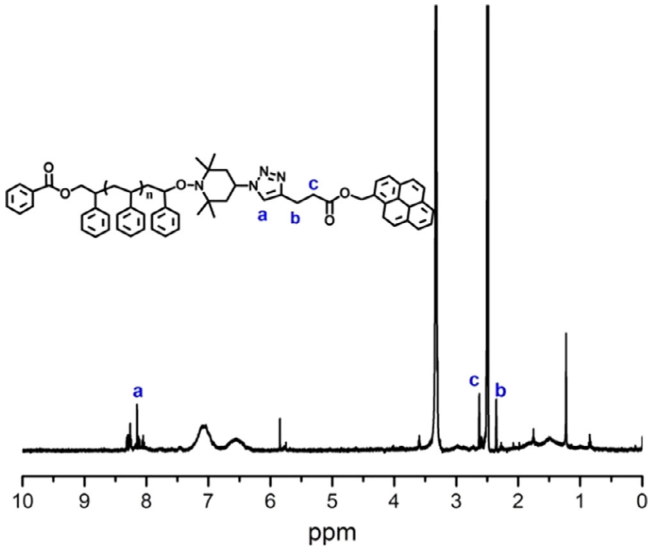


FIGURE 3 ^{1}H NMR spectrum of PS-TEMPO-Py [Color figure can be viewed at wileyonlinelibrary.com]

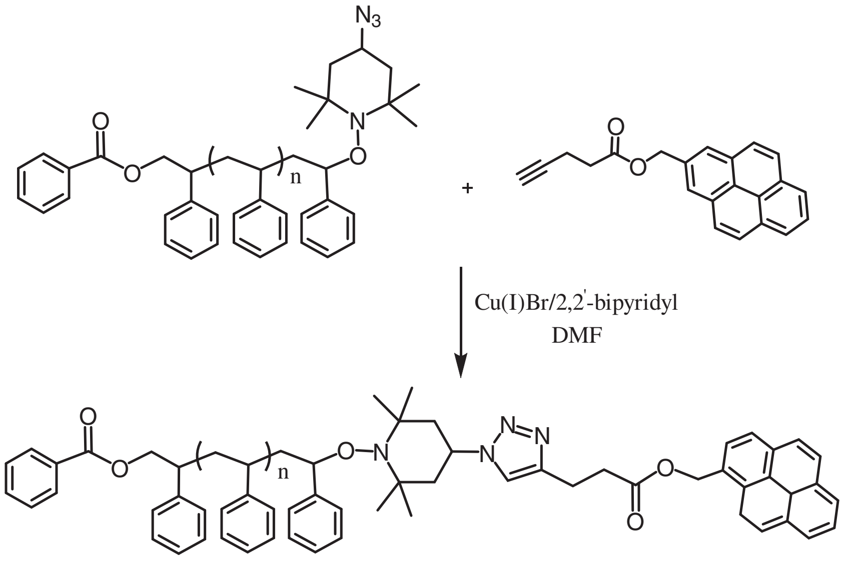
the mixture was stirred at 130 °C for 24 h. The resulting polymer was precipitated in methanol, (Conv: 82%). ^{1}H NMR [500 MHz, DMSO-d_6, δ]: 6.20–7.40 (Ar), 5.45 (d, CH_2), 5.21 (t, CH), 1.87 (t, CH_2), 1.74 (m, CH_2), 1.24 (s, CH_3). FTIR (cm^{-1}): 2100 (N_3 stretching).

Synthesis of Pyren-1-Ylmethyl Pent-4-Ynoate

1-Pyrenemethanol (1.0 g, 4.3 mmol), 4-pentynoic acid (0.5 g, 5.2 mmol), and DMAP (0.27 g, 2.15 mmol) were dissolved in 20 mL of dry DCM. After stirring at room temperature for 30 min, DCC (1.07 g, 5.15 mmol) dissolved in 10 mL of DCM was added to the solution. Reaction mixture was stirred overnight at room temperature. Then the solid residue was filtered, and the solvent was evaporated *in vacuo.* The crude product was purified by column chromatography over silica gel eluting with ethyl acetate/hexane (1:2) yielded as yellow solid (yield: 0.94 g; 70%). ^{1}H NMR [500 MHz, DMSO-d_6, δ]: 8.09–8.36 (Ar), 5.85 (s, CH_2), 2.82 (s, CH), 2.60 (t, CH_2), 2.44 (t, CH_2). ^{13}C NMR [125 MHz, DMSO-d_6, δ]: 174.3, 140.6, 132.2, 130.4, 129.6, 128.8, 126.5, 124.3, 123.05, 83.2, 70.2, 64.8, 33.1, 14.2.

Synthesis of Pyrene Functional Polystyrene (PS-TEMPO-Py) by CuAAC

PS-TEMPO-N_3 (45 mg, 0.025 mmol), pyren-1-ylmethyl pent-4-ynoate (10 mg, 0.038 mmol), catalyst (CuBr, 3.6 mg,



SCHEME 2 Synthesis of PS-TEMPO-Py.

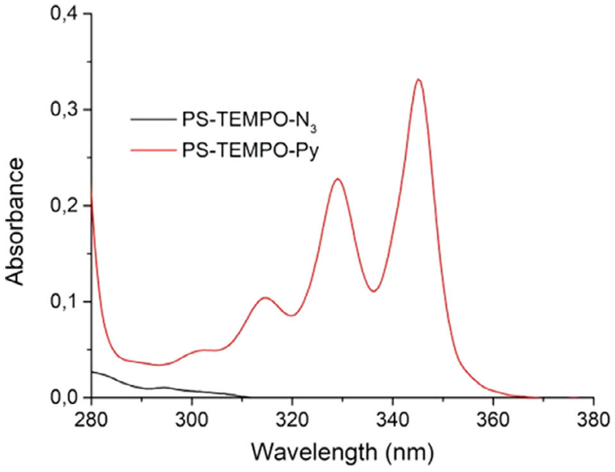


FIGURE 4 UV spectrum of PS-TEMPO-N_3 and PS-TEMPO-Py in DCM [Color figure can be viewed at wileyonlinelibrary.com]

0.025 mmol), ligand (2,2′-bipyridyl, 7.8 mg, 0.05 mmol), and 600 µl of DMF were placed in a Schlenk tube. The reaction mixture was degassed by three freeze–pump–thaw cycles and stirred at room temperature for 24 h, and the resulting polymer was precipitated in methanol. (M_n = 2150, PDI = 1.21 coupling efficiency 72%). ^{1}H NMR [500 MHz, DMSO-d_6, δ]: 7.9–8.3 (Ar, pyrene), 7.6 (CHN_3), 6.20–7.40 (Ar), 5.45 (d, CH_2), 5.19 (t, CH), 1.87 (t, CH_2), 1.76 (m, CH_2), 1.25 (s, CH_3).

Synthesis of TEMPO Functional Poly(ε-Caprolactone) (TEMPO-PCL)

Previously flamed Schlenk tube equipped with a magnetic stirring bar was filled with ε-CL (5.0 mL, 0.047 mol) in bulk using tin(II)-2-ethylhexanoate (0.01 mL, 0.03 mmol) as a catalyst and TEMPO-OH (0.270 g, 1.57 mmol) as an initiator was heated to 110 °C for 4 h. The mixture was diluted with THF and precipitated into an excess amount of cold methanol. The TEMPO-PCL was dried in a vacuum oven for 24 h. ($[M]_0/[I]_0 = 30$; $[I]_0/[cat]_0 = 50$; Conv: 26%, M_n = 8600, PDI = 1.37).

Synthesis of PEG-OTs

PEG-OMe (2 g, 1 mmol) was placed in round-bottom flask in 20 ml of DCM. NEt_3 (900 µl, 6 mmol) and TsCl (3.8 g, 20 mmol) were added to the flask under N_2 and stirred 96 h at room temperature. The reaction mixture was diluted with DCM and washed with saturated NH_4Cl, and the collected water phase was extracted with DCM. Combined organic phase was dried over $MgSO_4$, concentrated *in vacuo* and precipitated in cold diethyl ether (403 mg, M_n = 1900, PDI = 1.05). ^{1}H NMR [500 MHz, $CDCl_3$, δ,]: 7.30–8.01 (Ar), 3.59 (t, CH_2), 3.52 (t, CH_2), 3.41 (s, CH_3), 2.43 (s, CH_3).

Synthesis of TEMPO Functional Poly(Ethylene Glycol) (TEMPO-PEG)

NaH (≈60% in mineral oil) (24 mg, 0.598 mmol) was added to a solution of TEMPO-OH (87 mg, 0.505 mmol) in 5 ml DMF at 0 °C. After 1 h at 0 °C, solution of PEG-OTs (1 g, 0.46 mmol) in 5 ml DMF was added to the mixture over 10 min, and the reaction was heated to 60 °C for 2 h. The solvent was removed *in vacuo.* Residue dissolved in DCM and washed with water. Organic phase was dried over $MgSO_4$, concentrated *in vacuo* and precipitated in cold diethyl ether, and product was obtained as white solid (517 mg, M_n = 1800, PDI = 1.06). ^{1}H NMR [500 MHz, $CDCl_3$, $PhNHNH_2$, δ]: 3.56 (t, OCH_2), 3.52 (t, -O CH_2), 3.40 (s, -OCH_3), 3.30 (s, OCH), 1.61 (d, CH_2), 1.14 (s, CH_3). FT-IR (cm^{-1}): 2890, 2867, 1474, 1339, 1279, 1242, 1150, 1105, 1056, 950, 839, 655, 558.

Synthesis of PS-*b*-PCL

In a typical experiment, PS-TEMPO (100 mg, 0.056 mmol) and TEMPO-PCL (480 mg, 0.056 mmol) were placed in previously flamed Schlenk tube equipped with a magnetic stirring bar and dissolved in 4 ml of dry toluene and the mixture was heated to 130 °C and stirred 24 h. Resulting polymer was precipitated into methanol (270 mg, $M_{n,\ GPC}$ = 10949 g/mol, PDI = 1.23, coupling efficiency 62%). ^{1}H NMR [500 MHz, $CDCl_3$, δ,]: 6.50–7.43 (Ar), 5.46 (d, CH), 4.86 (d, CH), 3.67 (t, CH), 4.12 (t, CH_2), 2.32 (t, CH_2), 1.76 (d, CH_2), 1.66 (m, CH_2), 1.58 (m, CH_2), 1.29 (m, CH_2), 1.14 (s, CH_3).

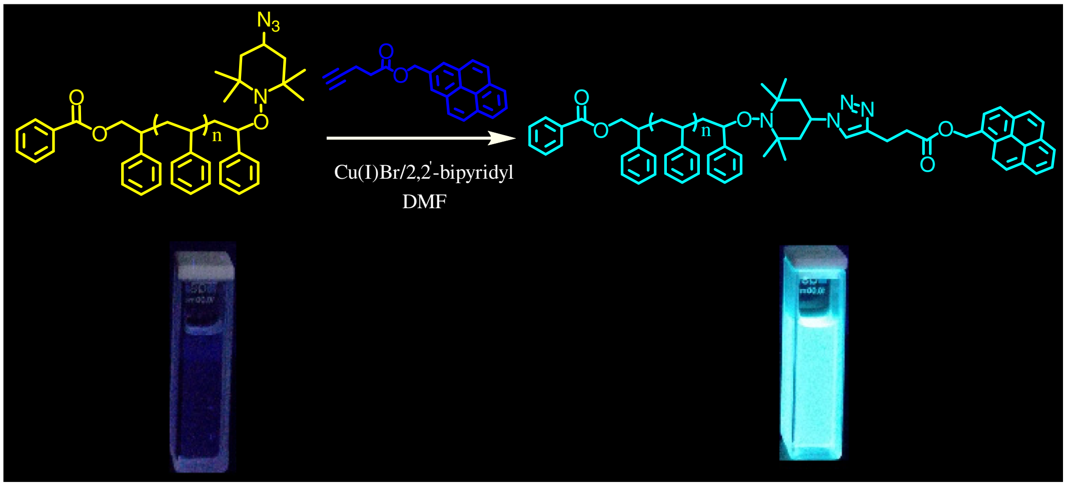
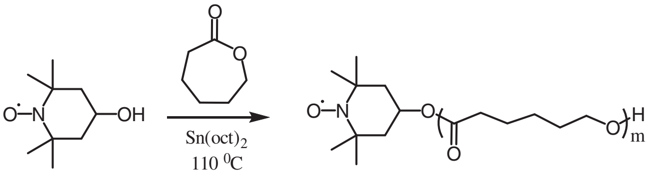


FIGURE 5 Photographs of PS-TEMPO-N_3 and PS-TEMPO-Py in DCM recorded with UV lamp irradiation at 366 nm [Color figure can be viewed at wileyonlinelibrary.com]



SCHEME 3 Synthesis of TEMPO-PCL.

Synthesis of PS-*b*-PEG

In a typical experiment, PS-TEMPO (100 mg, 0.056 mmol) and TEMPO-PEG (308 mg, 0.14 mmol) were in previously flamed Schlenk tube equipped with a magnetic stirring bar and dissolved in 4 ml of dry toluene, and the mixture was heated to 130 °C and stirred 24 h. Resulting polymer was precipitated into methanol (200 mg, $M_{n,\ GPC}$ = 7500 g/mol, PDI = 1.08 coupling efficiency 73%). ^{1}H NMR [500 MHz, $CDCl_3$, δ,]: 6.20–7.40 (Ar), 3.56 (t, OCH_2), 3.52 (t, -O CH_2), 1.76 (m, CH_2), 1.25 (s, CH_3).

RESULTS AND DISCUSSION

Firstly, PS-TEMPO was synthesized by conventional NMRP technique and characterized by spectral analysis. ^{1}H NMR spectrum of the PS-TEMPO clearly displays the characteristic peaks emerging from aromatic protons around 6.50–7.20 ppm. Methyl and methylene protons of TEMPO can be seen at 1.40 and 1.72 ppm. Unimodal molecular weight distribution of PS-TEMPO (M_n = 1800, PDI = 1.11) resulted from the controlled/living nature of the polymerization process.

In order to obtain functional polymers, hydroxyl, carboxylic acid, and azide functional TEMPO moieties were separately prepared and then incorporated to PS-TEMPO polymer (Scheme 1) by heating to 130 °C and stirring for 24 h in dry toluene. The products were analyzed by ^{1}H NMR and IR spectroscopic investigations. In each case, aromatic protons of the polystyrene segment are detectable between 6.40 and 7.20 ppm. The functional protons for PS-TEMPO, PS-TEMPO-OH, PS-TEMPO-COOH, and PS-TEMPO-N_3 are, respectively, labeled in Figure 1. As can be seen from the IR spectra presented in Figure 2, all the characteristic bands of the incorporated functional groups are evident. Typically, -OH peak in PS-TEMPO-OH is noted at 3490 cm^{-1}. The carbonyl bands belonging to the acid moiety in PS-TEMPO-COOH are detectable at 1510 and 1590 cm^{-1} and the corresponding azide band in PS-TEMPO-N_3 can be seen at 2100 cm^{-1}. These spectral investigations clearly confirm the successful functionalization.

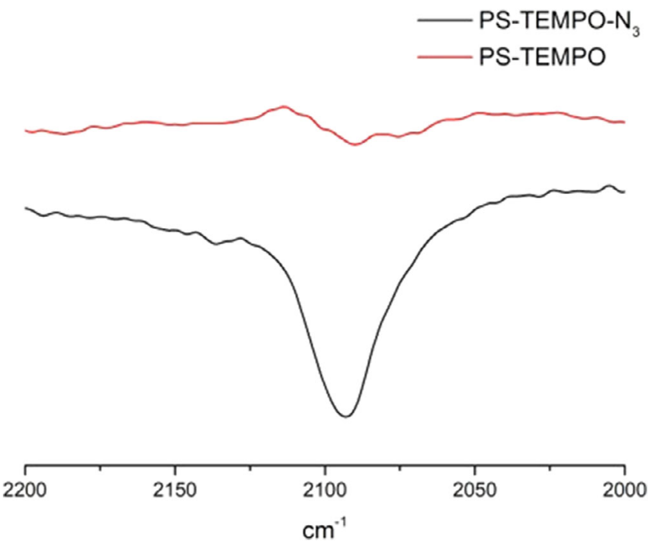
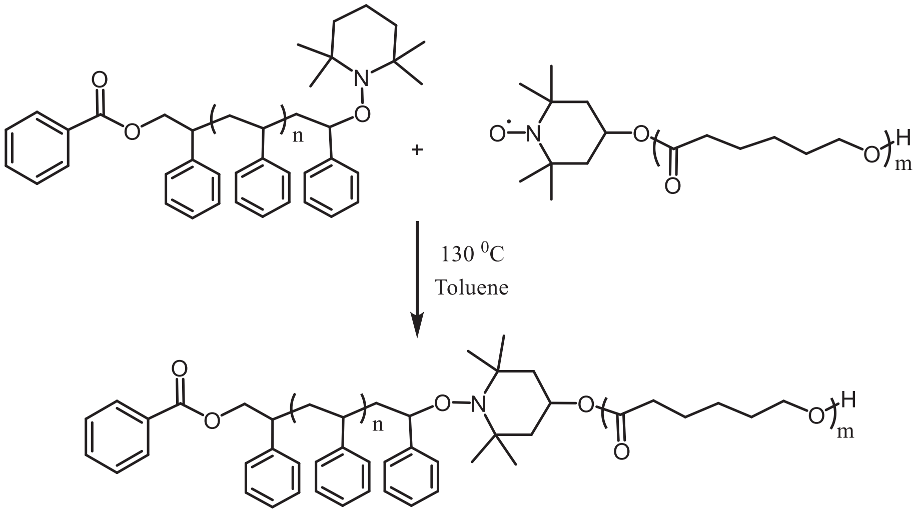


FIGURE 6 IR Spectra of PS-TEMPO-N_3 and PS-TEMPO [Color figure can be viewed at wileyonlinelibrary.com]

In order to demonstrate substantial reaction of the functional incorporated groups, a model click reaction between PS-TEMPO-N_3 and an alkyne containing pyrene moiety as a fluorescent compound was performed (Scheme 2). As can be seen from Figure 3, where ^{1}H NMR spectrum is presented, the aromatic protons of pyrene units appear at 7.9–8.5 ppm, and proton peak of triazole ring is observable at 8.15 ppm.



SCHEME 4 Synthesis of PS-*b*-PCL.

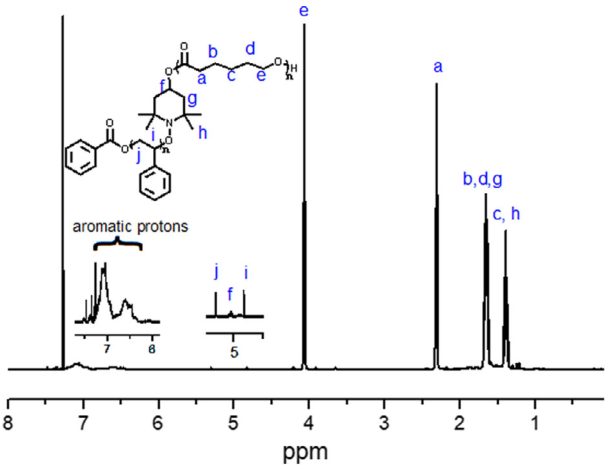
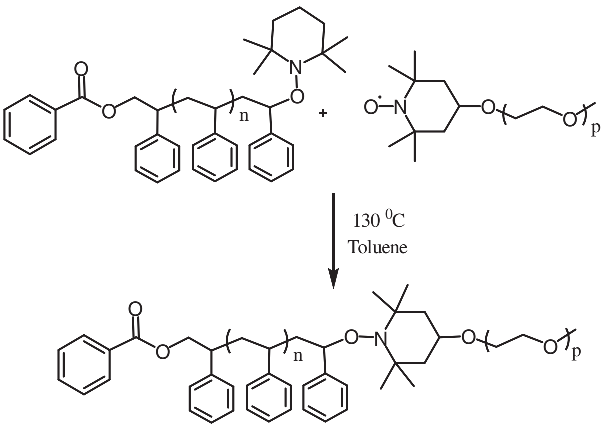


FIGURE 7 ^{1}H NMR spectrum of PS-*b*-PCL [Color figure can be viewed at wileyonlinelibrary.com]



SCHEME 5 Synthesis of PS-*b*-PEG.

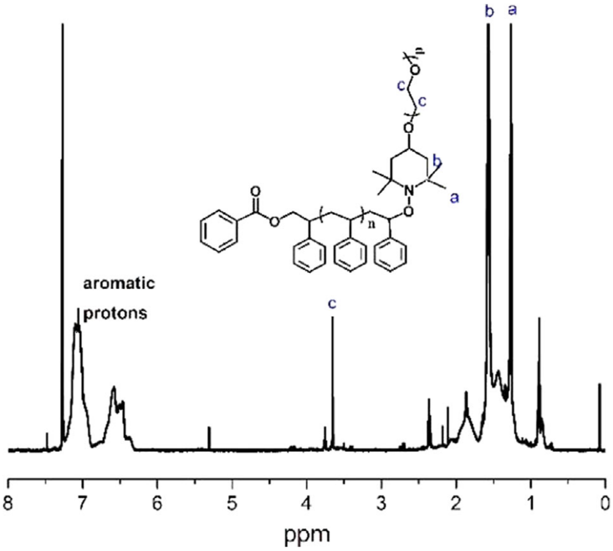


FIGURE 8 ^{1}H NMR spectrum of PS-*b*-PEG [Color figure can be viewed at wileyonlinelibrary.com]

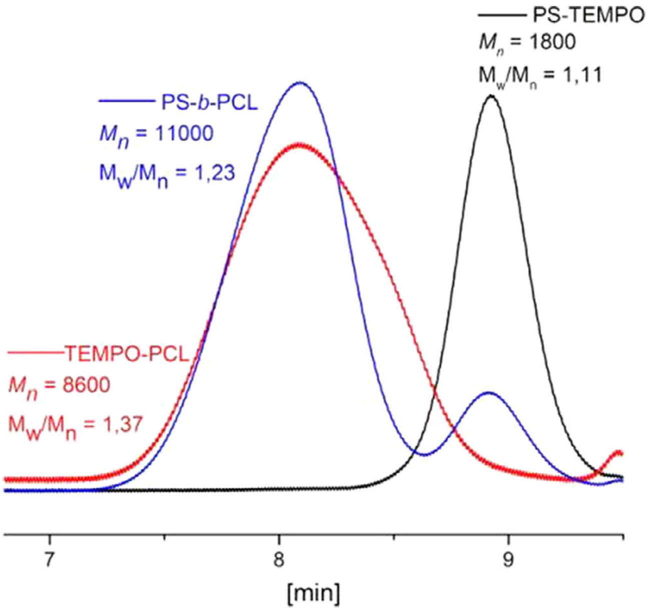


FIGURE 9 GPC chromatograms of the precursors PS-TEMPO, TEMPO-PCL, and PS-*b*-PCL [Color figure can be viewed at wileyonlinelibrary.com]

In the UV spectrum (Fig. 4) of the PS-TEMPO-Py polymer, the strong absorption peaks corresponding to the pyrene units incorporated were recorded at 339 and 356 nm.

The incorporation of pyrene moiety was further verified by the visual observation of the fluorescence emission of pyrene-modified polymer in DCM when irradiated with a UV lamp at 366 nm (Fig. 5).

In order to demonstrate the modularity of this process, PS-TEMPO-N_3 was dissolved in toluene and heated to 130 °C in the

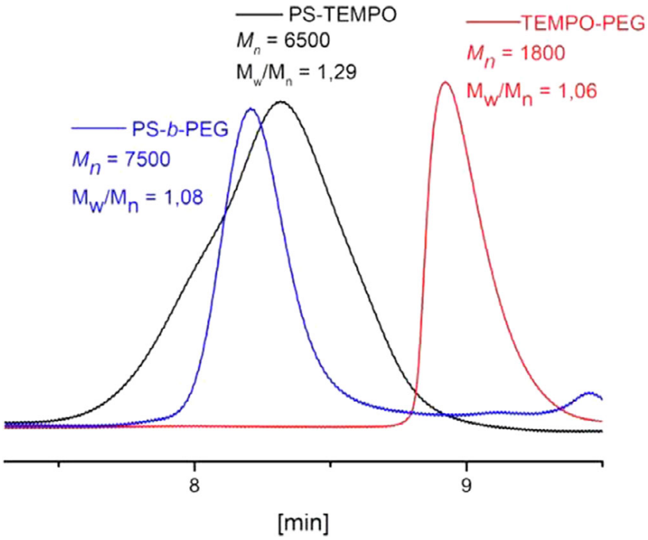


FIGURE 10 GPC chromatograms of the precursors PS-TEMPO, TEMPO-PEG, and PS-*b*-PEG [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Block copolymer formation[a] of PS-TEMPO with TEMPO-PCL and TEMPO-PEG in DCM

Precursor A	M_n $^{b}{}_{(A)}$ (g mol^{-1})	Precursor B	M_n $^{b}{}_{(B)}$ (g mol^{-1})	Block copolymer (C)	$M_n$$^{b}{}_{(C)}$ (g mol^{-1})
PS-TEMPO	1800	TEMPO-PCL	8600	PS-*b*-PCL	11000
PS-TEMPO	6500	TEMPO-PEG	1800	PS-*b*-PEG	7500

[a] Conducted at 130 °C for 24 h.

[b] Determined by GPC measurements according to polystyrene standards.

presence of excess TEMPO for 24 h. As can be seen from Figure 6, N_3 peak around 2100 cm^{-1} was disappeared, which clearly proves that the TEMPO units can be changed upon request.

Following the model reactions, similar process was applied to obtain block copolymers of polystyrene with poly(ε-caprolactone) and poly(ethylene glycol). First, TEMPO-PCL polymer was synthesized by the conventional ring opening polymerization (M_n = 8600, M_w/M_n = 1.37) (Scheme 3).

When equimolar amounts of PS-TEMPO (M_n = 1800, M_w/M_n = 1.11) and TEMPO-PCL (M_n = 8600, M_w/M_n = 1.37) was heated to 130 °C in dry toluene (Scheme 4), PS-*b*-PCL with higher molecular weight (M_n = 11000, M_w/M_n = 1.23) was readily formed and the structure of the resulting block copolymer was confirmed by ^{1}H NMR analysis (Fig. 7). The characteristic peaks emerging from PCL block were observed at 1.50–1.80 ppm and around 4.2 ppm.

The process was also applied to a structurally different polymer, namely TEMPO functionalized PEG. In the case of PS-*b*-PEG synthesis, commercially available PEG-OMe (M_n ~2,000) was used. First, PEG-OMe was tosylated and then tosyl group was replaced by TEMPO moiety. Since the unreacted PEG chains could be easily removed by precipitation in appropriate solvents, we used excess amount of PEG-TEMPO in comparison to the precursor PS-TEMPO. Under these experimental conditions, the corresponding PS-*b*-PEG block copolymer was obtained (Scheme 5). As can be seen from the ^{1}H NMR spectrum (Fig. 8), characteristic peaks of both PS and PEG segments were observed at 6.50–7.20 ppm and 3.71–3.92 ppm, respectively.

When higher and lower molecular weight compounds are compared in terms of their coupling efficiencies, the ones with lower molecular weight show better results. This situation can be regarded as a drawback for polymers with high molecular weights. Similar issue is also valid for the other coupling/ligation reactions. For example, while thiol-ene click reaction proceeds perfectly for low molar mass compounds, the analogous polymer-polymer reactions work with a limited success.[30]

The expected shift to the higher molecular weight region in the GPC chromatograms with for both cases was also observed (Figs. 9 and 10). The overall molecular weight characteristics of the precursor polymers and resulting block copolymers are presented in Table 1.

CONCLUSIONS

In conclusion, synthesis of functional polymers and block copolymers from structurally different monomers can simply be achieved by stable radical exchange reactions without the necessity of any catalysts. When polystyrene formed via NMRP technique and any other TEMPO functionalized low molar mass molecule or polymer chain is heated to 130 °C, functional polymers and block copolymers can be obtained in one step. This methodology provides a versatile route for the construction of various macromolecular architectures including graft and star copolymers by using suitably selected functional materials. Further studies in this line are now in progress.

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