Synthesis of Polystyrene-Based Random Copolymers with Balanced Number of Basic or Acidic Functional Groups

IVAYLO DIMITROV, KATJA JANKOVA, SØREN HVILSTED

Department of Chemical and Biochemical Engineering, Danish Polymer Centre, Technical University of Denmark, Building 423, DK-2800 Kgs. Lyngby, Denmark

Received 23 December 2009; accepted 11 February 2010
DOI: 10.1002/pola.23974
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Pairs of polystyrene-based random copolymers with balanced number of pendant basic or acidic groups were synthesized utilizing the template strategy. The same poly[(4-hydroxystyrene)-*ran*-styrene] was used as a template backbone for modification. Two different synthetic approaches for the functionalization were applied. The first one involved direct functionalization of the template backbone through alkylation of the phenolic groups with suitable reagents. The second modification approach was based on "click" chemistry, where the introduction of alkyne groups onto the template backbone was followed by copper-catalyzed 1,3 cycloaddition of aliphatic sulfonate- or amine-contaning azides. Both synthetic approaches proved to be highly efficient as evidenced by ^{1}H-NMR analyses. The thermal properties were evaluated by differential scanning calorimetry and thermal gravimetric analyses and were influenced by the type of functionality and the modification method. The ether-linked functional colopymers were thermally more stable than their "clicked" analogues. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 2044–2052, 2010

KEYWORDS: functionalization of polymers; polyelectrolytes; synthesis; thermal properties

INTRODUCTION

The cooperative formation of ionic bonds between two oppositely charged polyelectrolytes is a very versatile driving force for self-assembly.[1] The formed polyelectrolyte complexes (PECs) can be very effective for the delivery and release of active materials, such as DNA[2,3] and drugs,[4] immobilization of enzymes[5] or cells,[6] separation membranes,[7] and protein purification.[8] Oppositely charged polyelectrolytes have been used in the layer-by-layer assembly technique for the production of electrochemically enabled polyelectrolyte multilayer devices.[9] Acid-base polymer blend membranes for fuel cell applications obtained by mixing of polysulfonates and polybases have shown improved mechanical and thermal stability compared to the sulfonated polymers alone.[10,11] Matched pairs of copolymers with the same block length of polyanionic and polycationic segments have been synthesized by Harada and Kataoka through a ring-opening polymerization of *N*-carboxyanhydrides of oppositely charged α-aminoacids initiated by a polyoxyethylene macroinitiator[12] or derived from a platform block copolymer through modification reactions.[13] Other examples of the preparation of copolymer pairs with comparable content of opposite charges involve anionic polymerization and subsequent modification[14] or reversible addition-fragmentation chain transfer (RAFT) radical polymerization of suitable monomers.[15]

Recently, we utilized the template strategy to introduce pendant sulfonate groups onto highly hydrophobic fluorinated aromatic backbones.[16] Furthermore, the random copolymers of styrene and 4-hydroxystyrene were used as templates for the modification with aliphatic or aromatic carboxylic acid pendant groups.[17] In the latter case, the functionalization was performed through the highly efficient "click" chemistry approach based on copper catalyzed 1,3 cycloaddition of azides and alkynes (CuAAC).[18–22]

In attempt to overcome the inherent poor film forming properties of polystyrene-based sulfonated copolymers herein, we utilize the template strategy for the preparation of pairs of oppositely charged polymers with balanced content of acidic or basic pendant groups. Two different synthetic approaches for the modification of the same polymer backbone are presented. The first one relies on "click" chemistry, whereas the second one involves etherification reactions. The influence of the different functional groups and methods for preparation on the thermal properties of the oppositely charged copolymers is evaluated.

EXPERIMENTAL

Materials

All the reagent chemicals were purchased from Aldrich unless otherwise indicated. Styrene (S, 99%) was distilled

Additional Supporting Information may be found in the online version of this article. Correspondence to: S. Hvilsted (E-mail: sh@kt.dtu.dk)

under reduced pressure. 4-*tert*-Butoxystyrene (*t*BS, 99%) was passed through an inhibitor-removing column before use. α,α′-Azoisobutyronitrile (AIBN, 98%) was recrystallized from methanol. Xylene (Fisher Chemicals, 99%), tetrahydrofuran (THF, 99.9%), *N,N*-dimethylformamide (DMF, 99%), methanol (99.9%), and 1,4-dioxane (>99%) were purified and dried applying standard procedures. Di-*tert*-butyl dicarbonate (Fluka, >98%), 3-chloropropylamine hydrochloride (98%), 3-bromopropanesulfonic acid sodium salt (>99%), 2-chloro-*N,N*-dimethylethylamine hydrochloride (98%), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA, 99%), propargyl bromide (71.7 wt % in toluene), 18-crown-6 (99%), potassium carbonate (99%), tetrabutylammonium iodide (TBAI, ≥99%), potassium iodide (≥99%), sodium azide (99%), copper(I) bromide (CuBr, 98%), and 1,3-propanesultone (PrS, 98%) were used as received.

Poly[(4-hydroxystyrene)-*ran*-styrene] (PS-*ran*-PHS)

Poly[(4-hydroxystyrene)-*ran*-styrene] (PS-*ran*-PHS) was synthesized by free radical polymerization of styrene (S) and 4-*tert*-butoxystyrene (*t*BS) in xylene at 65 °C followed by deprotection to hydroxyl derivatives as previously described.[17] Random copolymer with composition of ∼20/80 mol % (HS/S) was obtained. SEC in THF (vs. polystyrene standards): M_n = 15,000, M_w/M_n = 1.72. FTIR (cm^{-1}): 3349 (O—H), 1225 (C_6H_4—O). ^{1}H-NMR (300 MHz, DMSO-d_6, δ, ppm): 9.0 (C_6H_4—O*H*), 7.25–6.85 (3H, C_6H_5), 6.85–6.15 (2H, C_6H_5 + C_6H_4—OH), 2.2–1.65 (C*H*—C_6H_4 + C*H*—C_6H_5), 1.65–1.1 (CH_2—CH—C_6H_4 + CH_2—C_6H_5).

Poly[4-(prop-2-ynoxy)styrene-*ran*-styrene] (PS-*ran*-PAS)

Poly[4-(prop-2-ynoxy)styrene-*ran*-styrene] (PS-*ran*-PAS) was obtained from PS-*ran*-PHS through a Williamson etherification with propargyl bromide.[23] SEC in THF (vs. polystyrene standards): M_n = 18,600, M_w/M_n = 1.73. FTIR (cm^{-1}): 3297 (C≡C—H), 1216 (C_6H_4—O). ^{1}H-NMR (300 MHz, DMSO-d_6, δ, ppm): 7.3–6.85 (3H, C_6H_5), 6.85–6.15 (2H, C_6H_5 + C_6H_4—O—CH_2), 4.67 (C_6H_4—O—CH_2), 3.51 (CH_2—C(*H*), 2.3–1.65 (C*H*—C_6H_4 + C*H*—C_6H_5), 1.65–1.0 (CH_2—CH—C_6H_4 + CH_2—C_6H_5).

Synthesis of *tert*-Butyl *N*-(3-Chloropropyl) carbamate (*Boc*-CPA)

Typically, 5 g of di-*tert*-butyl dicarbonate (22.91 mmol) and 2.98 g (22.91 mmol) of 3-chloropropylamine hydrochloride were dissolved in 10 mL of solvent mixture THF/water (1:1, v/v). The pH was adjusted to ∼9 by the addition of 1 M aqueous NaOH and the reaction mixture was stirred overnight at room temperature. The solution was acidified to pH ∼2 to 3 (10% $KHSO_4$) and the product was extracted with dichloromethane. The organic layer was washed several times with water, dried over Na_2SO_4, filtered, and the solvents were evaporated. Yield: 3.78 g (85%). FTIR (cm^{-1}): 1516 (*N*—H, urethane, amide II), 1686 (C=O—urethane, amide I), 3347 (*N*—H). ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 4.67 (N*H*), 3.58 (CH_2—Cl), 3.26 (NH—CH_2), 1.96 (CH_2—CH_2—CH_2), 1.43 (CH_3)$_3$.

Synthesis of 3-Azidopropanesulfonic Acid Sodium Salt (APS)

Sodium azide (0.72 g, 11.1 mmol) and 3-bromopropanesulfonic acid sodium salt (1 g, 4.44 mmol) were mixed in 30 mL of DMF and stirred under nitrogen overnight. The reaction mixture was concentrated, filtered, and most of the solvent was removed on a rotary evaporator. The product was precipitated in THF and dried. Yield: 0.8 g (96%). FTIR (cm^{-1}): 1055 and 1208 (O=S=O), 2103 (N^-=N^+=N). ^{1}H-NMR (300 MHz, D_2O, δ, ppm): 3.51 (N^-=N^+=*N*—CH_2), 3.02 (CH_2—SO_3^-), 2.04 (CH_2—CH_2—CH_2).

Synthesis of *tert*-Butyl *N*-(3-Azidopropyl) carbamate (*Boc*-APA)

Sodium azide (0.84 g, 12.91 mmol) and *tert*-butyl *N*-(3-chloropropyl) carbamate (1 g, 5.16 mmol) were stirred in 35 mL of DMF at 90 °C overnight under nitrogen. Most of the solvent was evaporated. The residue was diluted with 35 mL of dichloromethane and extracted with water (3 × 50 mL). The organic layer was dried over sodium sulfate, filtered, and the solvent was evaporated. Yield: 0.86 g (84%). FTIR (cm^{-1}): 1516 (*N*—H—urethane, amide II), 1686 (C=O—urethane, amide I), 2093 (N^-=N^+=N), 3347 (*N*—H). ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 4.66 (N*H*), 3.35 (CH_2—N=N^-=N^+), 3.21 (NH—CH_2), 1.78 (CH_2—CH_2—CH_2), 1.44 (CH_3)$_3$.

Synthesis of 2-Azido-*N,N*-dimethylethylamine (ADMEA)

The synthetic procedure was adapted from the literature.[24] Sodium azide (2.71 g, 41.65 mmol) and 2-chloro-*N,N*-dimethylethylamine hydrochloride (2 g, 13.88 mmol) were dissolved in 50 mL of water and stirred at 80 °C for 16 h. The reaction mixture was concentrated to ∼1/3 of the initial volume (The temperature of the water bath should not exceed 50 °C). Then it was cooled down (ice bath) and 50 mL of diethyl ether was added followed by the addition of 2 g of potassium hydroxide on portions keeping the temperature below 10 °C. The mixture was stirred vigorously for 30 min. The organic layer was separated and the aqueous phase was extracted with diethyl ether (2 × 25 mL). The combined organic layers were dried over sodium sulfate and the solvent was evaporated. Yield: 1.1 g (70%). FTIR (cm^{-1}): 2107 (N^-=N^+=N), 2772 and 2833 (—N— (CH_3)$_2$). ^{1}H-NMR (300 MHz, DMSO-d_6, δ, ppm): 3.33 (N^-=N^+=*N*—CH_2), 2.44 (CH_2—N), 2.18 (N—(CH_3)$_2$).

Synthesis of Basic and Acidic Copolymers via Williamson-Type Etherification or Sulfoalkylation

*Polystyrene-Based Copolymer with Randomly Distributed Primary Amine Pendant Groups (PS-*ran*-PAPS)*

A solution of PS-*ran*-PHS (1 g, 1.95 mmol OH-groups), *Boc*-CPA (0.56 g, 2.9 mmol), potassium carbonate (0.67 g, 4.88 mmol), 18-crown-6 (0.076 g, 0.29 mmol), TBAI (0.11 g, 029 mmol), and potassium iodide (0.032 g, 0.195 mmol) in 15 mL of THF was refluxed for 24 h. The solution was filtered and washed consecutively with saturated aqueous sodium hydrogen carbonate and brine. Then, it was dried over magnesium sulfate, concentrated and the polymer was precipitated in methanol. Yield: 1 g (77%). ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 7.25–6.80 (3H, C_6H_5), 6.80–6.20 (2H, C_6H_5 +

C_6H_4—O—CH_2), 4.82 (N*H*), 3.93 (C_6H_4—O—CH_2), 3.32 (NH—CH_2), 1.94 (CH_2—CH_2—CH_2), 1.46 (CH_3)$_3$, 2.2–1.65 (C*H*—C_6H_4 + C*H*—C_6H_5), 1.65–1.1 (CH_2—CH—C_6H_4 + CH_2—C_6H_5).

Deprotection Procedure. The *Boc*-protected copolymer (0.8 g) was dissolved in 13 mL of THF followed by the addition of 1.3 mL concentrated HCl. The mixture was refluxed overnight. The clear solution was concentrated and the polymer was precipitated in water. After several washings with water, the product was stirred overnight in 1 M NaOH (15 mL), isolated, and washed extensively with water. Yield: 0.56 g (82%). ^{1}H-NMR (300 MHz, DMSO-d_6, δ, ppm): 7.3–6.82 (3H, C_6H_5), 6.82–6.15 (2H, C_6H_5 + C_6H_4—O—CH_2), 3.92 (C_6H_4—O—CH_2), 2.94 (CH_2—NH_2), 1.98 (CH_2—CH_2—CH_2), 2.1–1.65 (C*H*—C_6H_4 + C*H*—C_6H_5), 1.65–1.0 (CH_2—CH—C_6H_4 + CH_2—C_6H_5).

*Polystyrene-Based Copolymer with Randomly Distributed Sulfonic Acid Pendant Groups (PS-*ran*-PSPS)*

Sodium hydroxide (0.044 g, 1.11 mmol) was dissolved in 34 mL of methanol. Then PS-*ran*-PHS (0.4 g, 0.74 mmol OH-groups) was added and dissolved completely in the alkaline solution. After stirring at room temperature for 30 min, a solution of PrS (0.14 g, 1.11 mmol) in 1.3 mL of dioxane was added. The final solution was refluxed for 48 h. The reaction mixture was poured in dichloromethane. The polymer precipitated and was washed with another portion of dichloromethane and dried. The product was washed extensively with water. Yield: 0.45 g (88%). FTIR (cm^{-1}): 1195 and 1050 (O=S=O). ^{1}H-NMR (300 MHz, DMSO-d_6, δ, ppm): 7.3–6.82 (3H, C_6H_5), 6.82–6.10 (2H, C_6H_5 + C_6H_4—O—CH_2), 3.92 (C_6H_4—O—CH_2), 2.58 (CH_2—$SO_3^-Na^+$), 2.0 (CH_2—CH_2—CH_2), 2.1–1.65 (C*H*—C_6H_4 + C*H*—C_6H_5), 1.65–1.0 (CH_2—CH—C_6H_4 + CH_2—C_6H_5).

The sodium sulfonate pendant groups in the copolymer were converted to sulfonic acids by treatment with 1 M HCl for 12 h at room temperature followed by extensive washings with water. ^{1}H-NMR (300 MHz, DMSO-d_6, δ, ppm): 2.68 (CH_2—SO_3H).

Synthesis of Basic and Acidic Copolymers via "Click" Chemistry

*Polystyrene-Based Copolymer with "Clicked" Primary Amine Pendant Groups (PS-*ran*-PAPScl)*

PS-*ran*-PAS (0.65 g, 1.13 mmol alkyne groups), 0.065 g (0.45 mmol) of CuBr and 0.078 mL (0.45 mmol) of PMDETA were mixed in 8 mL of DMF. *Boc*-APA (0.29 g, 1.46 mmol) was dissolved in 4 mL of THF and added to the reaction mixture. The solution was degassed and backfilled with nitrogen thrice and was stirred at 60 °C overnight. The solvents were evaporated. The residue was dissolved in small amount of dichloromethane and the product was precipitated in water to give yellow powder after drying. Yield: 0.83 g (94%). ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 7.68 (C=C*H*—N), 7.25–6.82 (3H, C_6H_5), 6.82–6.15 (2H, C_6H_5 + C_6H_4—O—CH_2), 5.1 (C_6H_4—O—CH_2), 4.87 (N*H*), 4.4 (*N*—CH_2—CH_2), 3.14 (NH—CH_2), 2.08 (CH_2—CH_2—CH_2), 1.45 (CH_3)$_3$, 2.1–1.6 (C*H*—C_6H_4 + C*H*—C_6H_5), 1.6–1.1 (CH_2—CH—C_6H_4 + CH_2—C_6H_5).

The *Boc*-protected product was deprotected as described for PS-*ran*-PAPS. ^{1}H-NMR (300 MHz, DMSO-d_6, δ, ppm): 8.17 (C=C*H*—N), 7.3–6.85 (3H, C_6H_5), 6.85–6.2 (2H, C_6H_5 + C_6H_4—O—CH_2), 5.03 (C_6H_4—O—CH_2), 4.4 (*N*—CH_2—CH_2), 3.0 (CH_2—NH_2), 1.86 (CH_2—CH_2—CH_2), 2.1–1.62 (C*H*—C_6H_4 + C*H*—C_6H_5), 1.62–1.0 (CH_2—CH—C_6H_4 + CH_2—C_6H_5).

*Polystyrene-Based Copolymer with "Clicked" Tertiary Amine Pendant Groups (PS-*ran*-PDMAEScl)*

PS-*ran*-PAS (1.06 g, 1.93 mmol alkyne groups) and CuBr (0.11 g, 0.77 mmol) were dissolved in 8 mL of DMF followed by the addition of ADMEA (044 g, 3.86 mmol) solution in 4 mL of DMF. The reaction mixture was degassed and backfilled with nitrogen thrice and was stirred overnight at 60 °C. Then it was concentrated and the polymer was precipitated in 10% HCl and extensively washed with water. The yellow product was stirred in 1 M NaOH for 30 min and washed with water. Yield: 1.15 g (89%). ^{1}H-NMR (300 MHz, DMSO-d_6, δ, ppm): 8.21 (C=C*H*—N), 7.35–6.90 (3H, C_6H_5), 6.90–6.15 (2H, C_6H_5 + C_6H_4—O—CH_2), 5.08 (C_6H_4—O—CH_2), 4.48 (*N*—CH_2—CH_2), 2.70 (*N*—CH_2—CH_2—N— (CH_3)$_2$), 2.18 (CH_3)$_2$, 2.1–1.65 (C*H*—C_6H_4 + C*H*—C_6H_5), 1.65–1.10 (CH_2—CH—C_6H_4 + CH_2—C_6H_5).

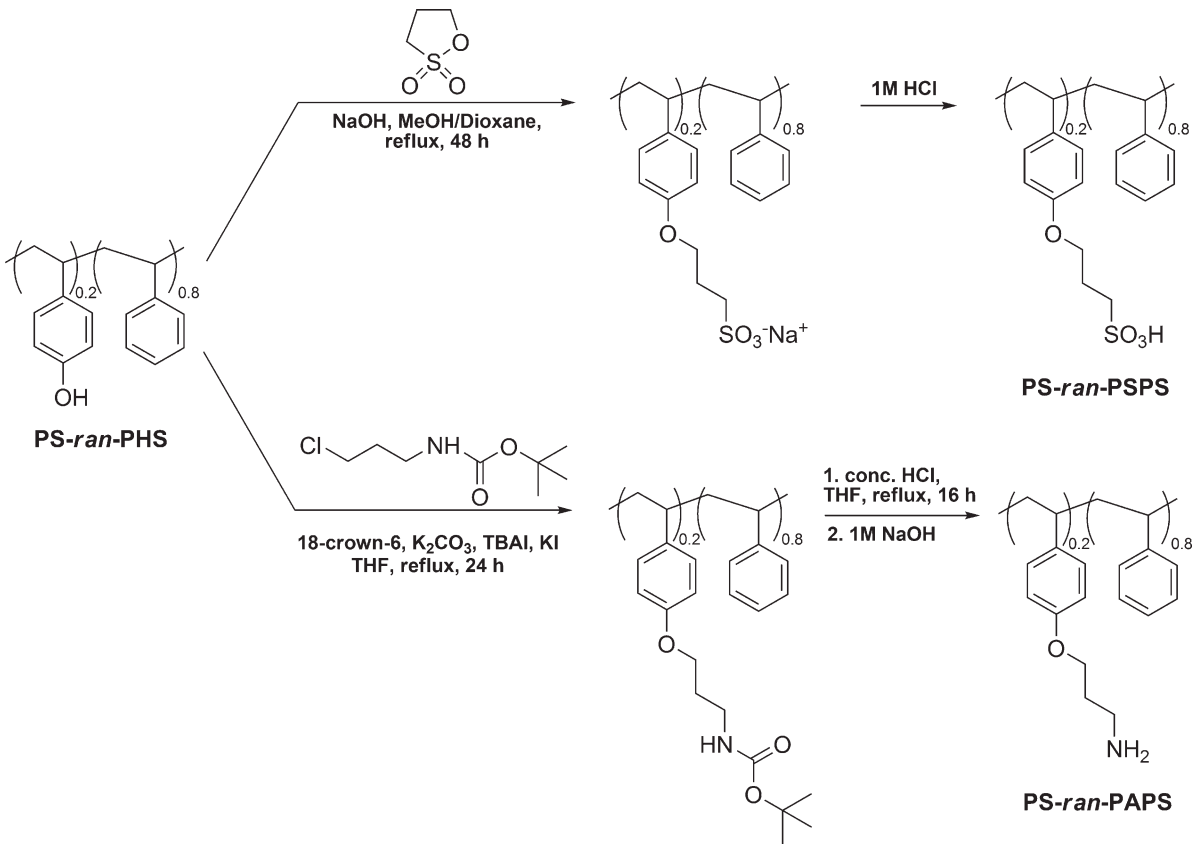
*Polystyrene-Based Copolymer with "Clicked" Sulfonic Acid Pendant Groups (PS-*ran*-PSPScl)*

PS-*ran*-PAS (0.65 g, 1.13 mmol alkyne groups), APS (0.27 g, 1.46 mmol), and CuBr (0.065 g, 0.45 mmol) were mixed in 8 mL of DMF. The dark-brown solution was degassed and backfilled with nitrogen thrice and stirred overnight at 60 °C. The product precipitated from the DMF solution. It was diluted with DMF and a few drops of 5 M NaOH were added. The mixture was stirred at room temperature for 3 h until complete dissolution of the product. The solvent was evaporated and the residue was washed extensively with water. Then, it was dried to give a dark-brown powder. Yield: 0.64 g (74%). FTIR (cm^{-1}): 1211 and 1045 (O=S=O). ^{1}H-NMR (300 MHz, DMSO-d_6, δ, ppm): 8.21 (C=C*H*—N), 7.4–6.85 (3H, C_6H_5), 6.85–6.15 (2H, C_6H_5 + C_6H_4—O—CH_2), 5.03 (C_6H_4—O—CH_2), 4.48 (*N*—CH_2—CH_2), 2.45 (CH_2—$SO_3^-Na^+$), 2.13 (CH_2—CH_2—CH_2), 2.1–1.62 (C*H*—C_6H_4 + C*H*—C_6H_5), 1.62–1.0 (CH_2—CH—C_6H_4 + CH_2—C_6H_5).

The polymer was redissolved in DMF at 70 °C and a few drops of 10% HCl were added. The solution became yellow. The solvent was evaporated and the residue was washed extensively with water to give a pale yellow powder after drying. ^{1}H-NMR (300 MHz, DMSO-d_6, δ, ppm): 2.54 (CH_2—SO_3H).

Characterization

^{1}H-NMR spectra were recorded on a Bruker 300 MHz spectrometer using $CDCl_3$, D_2O or DMSO-d_6 as solvents. Size exclusion chromatography (SEC) was performed in THF at room temperature at a flow rate of 1.0 mL/min on a set of PL guard and 2 PL gel mixed D columns (Polymer Laboratories), calibrated versus polystyrene narrow molar mass



SCHEME 1 Synthesis of polystyrene-based acidic and basic copolymers via sulfopropylation and Williamson-type etherification.

standards. Infrared spectra were recorded on a PerkinElmer Spectrum One model 2000 Fourier transform infrared system with a universal attenuated total reflection sampling accessory on a ZnSe/diamond composite. Thermal analyses were carried out on a differential scanning calorimeter DSC Q1000 (TA Instruments) in a temperature range of 25–200 °C at a heating and cooling rate of 10 °C/min under nitrogen. The glass transition temperatures (T_g) were determined during the second heating cycle at the inflection point of the thermal transition. Thermogravimetric analyses (TGA) were performed on a TGA Q500 instrument measuring the samples' total weight loss from 25 to 600 °C at a rate of 5 °C/min under a nitrogen flow of 90 mL/min.

RESULTS AND DISCUSSION

A polystyrene-based copolymer with ~20 mol % randomly distributed hydroxyl groups was used as a template for all modifications. The copolymer was synthesized by conventional free radical polymerization of S and *t*BS, followed by deprotection of *t*BS-units to *p*-hydroxystyrene- derivatives. As already demonstrated, the copolymer reactivity ratios are close to unity affording the formation of random copolymer architecture throughout the entire conversion range.[17]

To obtain copolymers with balanced number of acidic or basic groups, two approaches involving highly efficient modification steps were applied. The first one is based on etherification reactions, whereas the second one relied on azide-alkyne cycloaddition "click" chemistry.

Etherification Reactions

Different alkylating reagents were used to attach pendant functional groups onto the hydroxyl-functionalized template backbone (Scheme 1).

Basic Copolymers via Williamson-Type Etherification

A classical Williamson reaction between phenoxides and aminoalkyl halides was applied to obtain polystyrene-based copolymers with randomly distributed pendant primary amine groups (Scheme 1). Because of the rather forcing reaction conditions the primary amine groups in the alkylating reagent 3-chloropropyl amine were pacified through a *Boc*-protection. The hydroxyl groups in PS-*ran*-PHS were converted into phenoxides *in situ* by the use of potassium carbonate. The reaction rate was increased by the addition of KI. The salt undergoes halide exchange with the chloride to yield a more reactive alkylating reagent. Finally, TBAI and crown ether were added to form softer counter-ions for the alkoxides. The reaction was performed in THF and was completed in 24 h. The *Boc*-protection of the primary amine groups was removed by acidic treatment of the polymer and the primary amine groups were recovered in 1 M NaOH. The full conversion of hydroxyl into aminopropyl groups was evidenced by ^{1}H-NMR in $CDCl_3$ for the protected derivative and

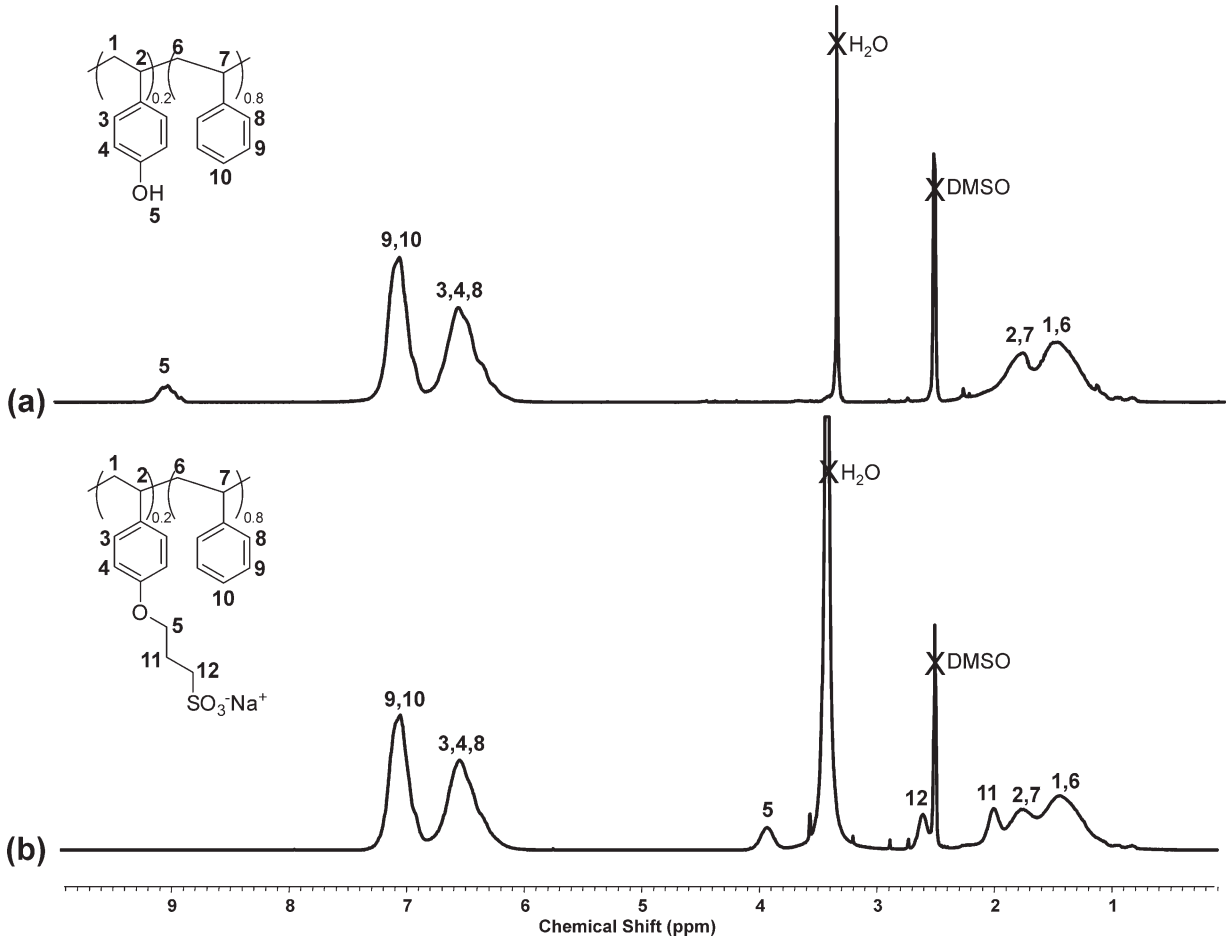


FIGURE 1 H-NMR spectra in DMSO-d_6 of (a) PS-*ran*-PHS precursor and (b) sulfopropylated copolymer PS-*ran*-PSPS.

in DMSO-d_6 for the basic copolymer (see Supporting Information).

Acidic Copolymers via Sulfopropylation

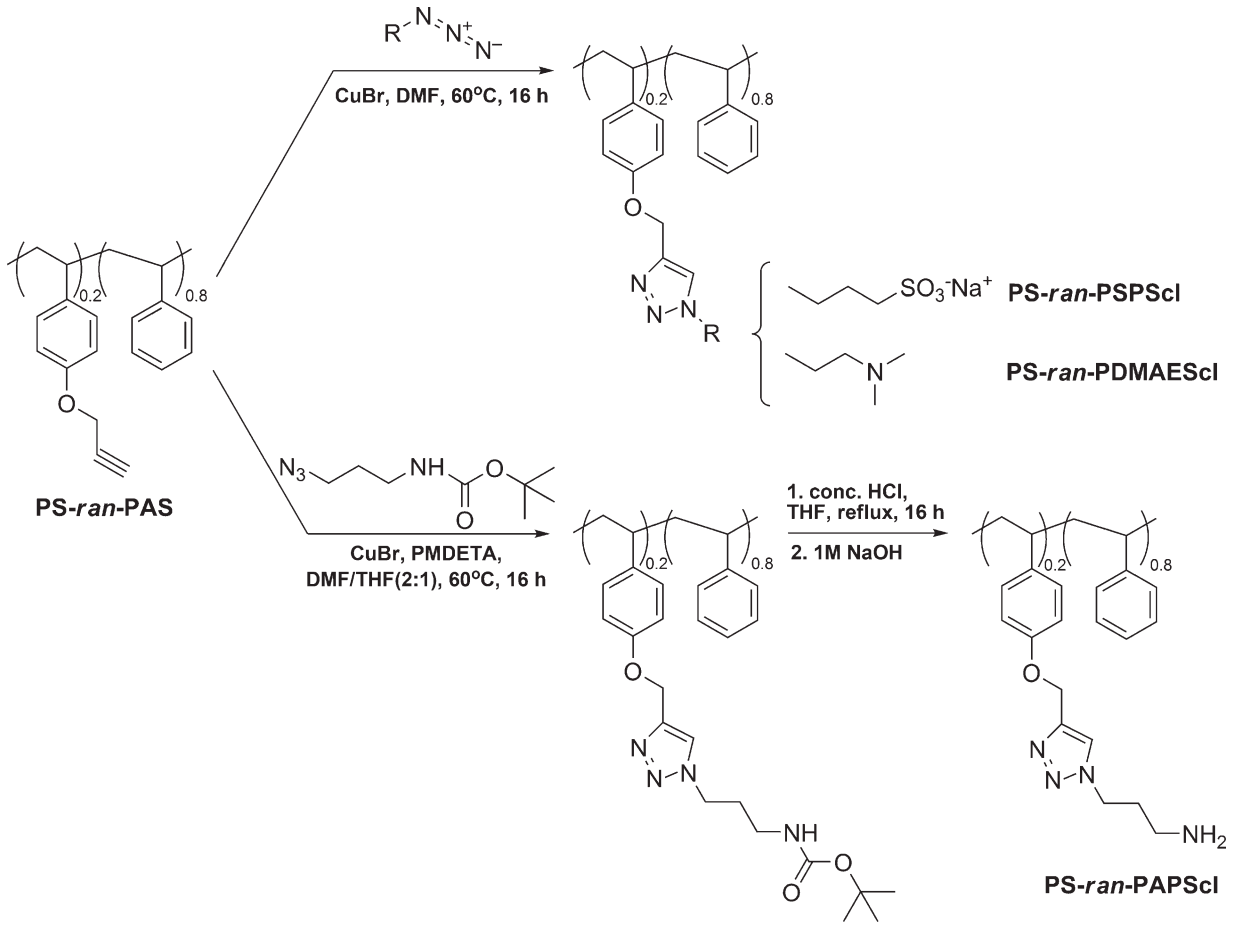
We have recently demonstrated that fluorinated aromatic copolymers of random and block architecture containing hydroxyl groups in *p*-position of the aromatic ring can be successfully sulfopropylated through a nucleophilic ring opening reaction of 1,3-propane sultone.[16] Here, we tested this approach on poly[(4-hydroxystyrene)-*ran*-styrene] in an attempt to form the same number and density of acidic pendant groups as for the basic copolymer, moreover with the same length of the alkyl spacer (Scheme 1). The polymer backbone was activated in methanolic solution of NaOH followed by the addition of 0.1 mol excess of PrS (Scheme 1). The reaction efficiency was confirmed by ^{1}H-NMR analysis in DMSO-d_6 (Fig. 1). The resonance for the phenolic proton at 9.0 ppm has completely disappeared in the spectrum of the product, whereas three new resonances at 3.92, 2.58, and 2.0 ppm corresponding to one oxymethylene and two methylene protons from the attached sulfopropyl side groups appeared. After the conversion of sodium sulfonate groups into sulfonic acids, the resonance corresponding to the neighboring methylene protons shifted from 2.58 to 2.68 ppm.

Basic and Acidic Copolymers via "Click" Chemistry

The "click" chemistry approach was utilized as an alternative for the preparation of copolymers with balanced basic and acidic functionalities. The principal synthetic route is shown in Scheme 2. The polystyrene-based alkyne-functionalized backbone was synthesized as previously described.[23] Acidic and tertiary amine-containing azides were synthesized from the corresponding commercially available functional alkyl halides. The primary amine-containing alkylazide was prepared from the *Boc*-protected chloropropylamine. It should be noted that due to the highly specific character of the alkyne-azide "click" reaction in general there is no need to protect the primary amine group in the azide reagent. We used the *Boc*-protected derivative because it was already prepared for the Williamson etherification and it was easier to handle during the azide preparation from a safety point of view.

Basic Copolymers

The click reaction of tertiary amine alkylazide was performed in DMF and was completed after 16 h (Scheme 2). The high efficiency of the modification was proved by ^{1}H-NMR analysis in DMSO-d_6 (Fig. 2). The alkyne proton resonance at 3.51 ppm has completely disappeared from the spectrum of the product and a new resonance at 8.21 ppm



SCHEME 2 Synthesis of polystyrene-based acidic and basic copolymers via "click" chemistry.

characteristic for the proton in the triazole ring appeared. The resonances at 4.48, 2.70, and 2.18 ppm corresponding to the methylene and methyl protons from the attached dimethylaminoethyl group are also clearly visible. The relative intensities of all these protons and the oxymethylene protons at 5.08 ppm from the alkyne precursor suggest complete functionalization. In the case where a *Boc*-protected aminoalkylazide was used, the click reaction was performed in a solvent mixture DMF/THF. The final reaction step involved removal of the protecting groups by acid treatment and the primary amine groups were recovered in 1 M NaOH. ^{1}H-NMR analyses both in $CDCl_3$ for the *Boc*-protected product and in DMSO-d_6 for the primary amine-containing copolymer confirmed the quantitative modification (see Supporting Information).

Acidic Copolymers

Polystyrene-based copolymers with randomly distributed pendant sulfonic acid groups were additionally synthesized applying the "click" chemistry approach. The copolymers can be considered as analogues to those obtained via Williamson synthesis. The only difference is the presence of the methylene-linked triazole ring in the latter. Azidopropanesulfonate was "clicked" with high efficiency to the alkyne-functionalized backbone PS-*ran*-PAS in DMF as a solvent. Upon the reaction completion, the product precipitated from the solution and after isolation became practically insoluble in common organic solvents. A similar phenomenon has been observed by Ryu and Zhao[25] who attempted to "click" azidoacetic acid onto alkyne-functionalized calix[4]-arene. The authors explain the formation of insoluble complex mixtures with possible homocoupling of alkynes as a side reaction. In our case, we believe that the reason for the formation of insoluble product is the strong intermolecular complexation between the sulfonate groups and the formed triazole rings. To destroy the complexes, the reaction mixture was diluted with DMF and a few drops of 5 M NaOH were added. The mixture was stirred at room temperature and product dissolved completely. After this treatment, the isolated polymer is soluble in DMF and DMSO at 70 °C and stays in solution upon cooling. ^{1}H-NMR analysis in DMSO-d_6 confirmed the completeness of the click reaction (see Supporting Information). The resonances characteristic for the protons from the sulfopropyl group at 4.48, 2.45, and 2.13 ppm and for the triazole proton at 8.21 ppm are clearly visible. Moreover, their relative intensities and the integral area of oxymethylene protons at 5.03 ppm from the backbone confirm the high efficiency of the "click" reaction. The sodium sulfonate pendant groups were converted into acids by treatment of the polymer solution in DMF with 10% HCl. After this

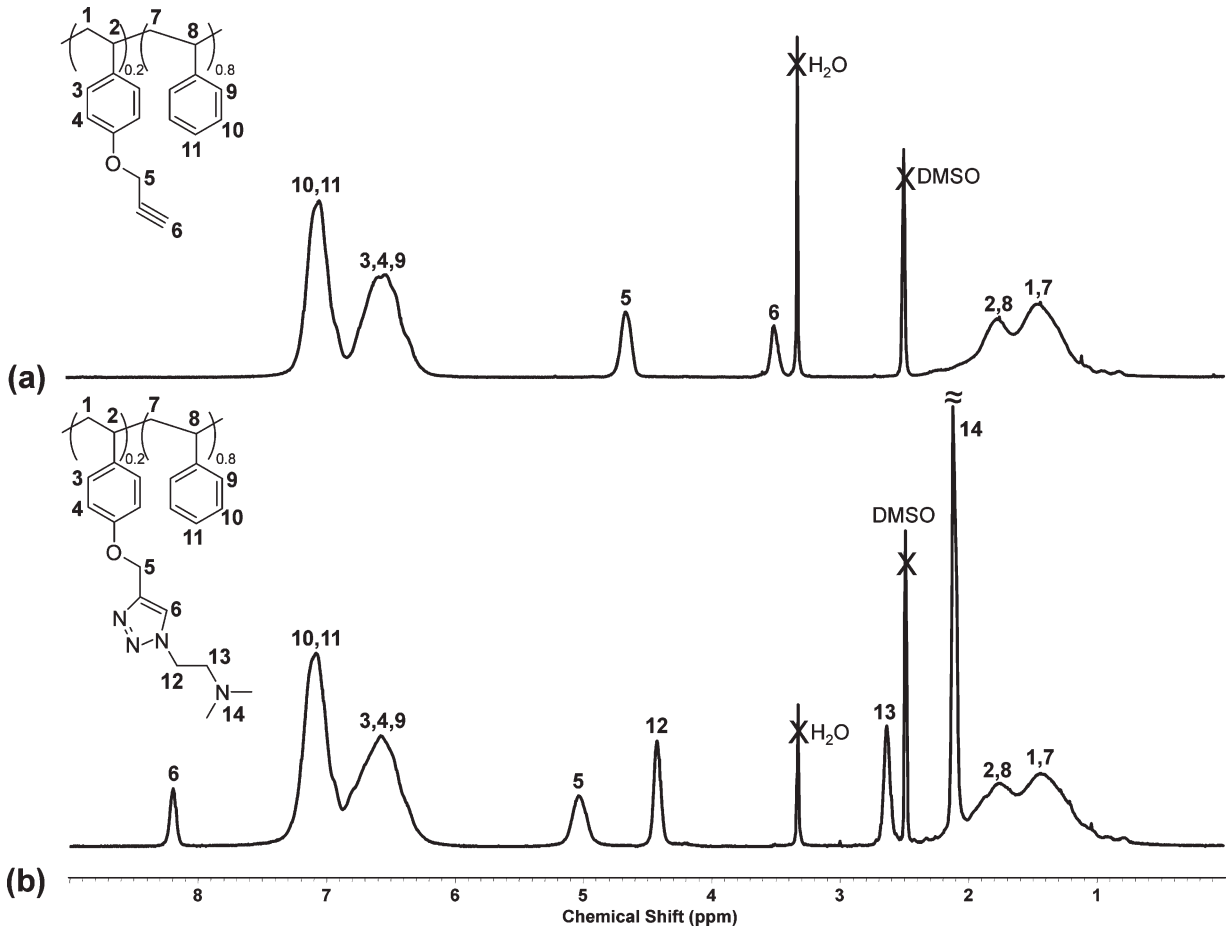


FIGURE 2 ^{1}H-NMR spectra in DMSO-d_6 of (a) alkyne-functionalized precursor PS-*ran*-PAS and (b) copolymer with "clicked" tertiary amine pendant groups PS-*ran*-PDMAESCl.

treatment, the polymers dissolve in DMF and DMSO even at room temperature. A similar behavior has already been observed for the fluorinated aromatic copolymers with sulfopropylated blocks.[16]

Thermal Properties

The thermal properties of the precursor copolymers and those of the products functionalized by different methods products were evaluated by their T_g and thermal decomposition (T_d) data (Table 1) measured by DSC and TGA, respectively. The glass transition depends on backbone functionalization. The initial T_g of 94 °C for the *t*-butoxy derivative increased to 113 °C after the deprotection to hydroxyl groups. Further modification with alkyne groups decreases the T_g to 88 °C. Similar results have previously been obtained for the corresponding random block copolymers with 25 mol % functional styrene.[17] Moreover, it was also demonstrated that increasing the amount of functionality in the random copolymers afforded a drastic change in T_g. Whereas T_g of the hydroxyl containing block copolymers increased up to 169 °C for 100% OH, most probably due to hydrogen bonding, the T_g of the prop-2-ynyl samples dropped down to 65 °C for the 100% alkyne, which could be due to internal plasticization. In the current investigation, "clicking" of same level of basic or acidic pendant groups also affects the T_g of copolymers. Although the presence of tertiary amine groups does not change the T_g, the same amount of primary aminopropyl groups leads to a 16° increase compared with the alkyne derivative. There is a significant increase in the T_g up to 175 °C when propylsulfonic acid groups are "clicked" (see Supporting Information). This is a much higher glass transition temperature than the previously reported value (88 °C) for the aliphatic carboxylic acid substituted backbone with comparable degree of functionalization.[17] The difference could be attributed to the shorter aliphatic chain of the sulfonate pendant groups (weaker plasticizing effect) and hydrogen bonding. The T_g values for the oppositely charged copolymer pairs obtained through etherification reactions are somewhat lower than those for the "clicked" copolymers with the same pendant groups. Most likely this is due to the presence of a bulky triazole ring in each pendant group of the latter, leading to an increased rigidity.

The thermal stability of the precursor functional copolymers increases from 318 °C for the *t*-butoxy derivative through 376 °C for the hydroxyl containing polymer to 403 °C for the alkyne functionalized backbone (Table 1). The "clicked"

functional copolymers exhibit lower thermal stability. Those with pendant amine groups start to decompose just above 360 °C, whereas the copolymers with "clicked" sulfopropyl groups start to decompose at 323 °C. Conversion of the sodium sulfonate groups into sulfonic acids leads to thermally less stable products which is consistent with the results obtained by other research groups.[26,27] All copolymers functionalized with pendant groups show a two-step degradation pattern. Typical TGA curves for the alkyne functionalized precursor and the corresponding tertiary amine "clicked" copolymer are presented in Figure 3. The first weight loss correlates with the content of the side groups, whereas the second one is attributed to the degradation of the backbone.

The amine and sodium sulfonate functional copolymers obtained through etherification reactions exhibit higher thermal stability compared to their "clicked" analogues (Table 1). Most likely, this is due to the earlier cleavage of the N—CH_2 bond in the latter rather than breakage of the triazole ring itself which is thermally more stable.[28] Moreover, the average energies for C—N and C—O bonds are 305 and 358 kJ/mol, respectively, indicating that the cleavage of the "clicked" pendant groups would be easier than that of their ether-linked analogues.

On the contrary, conversion of sulfonates to sulfonic acid groups leads to overall decrease in thermal stability with higher values for the "clicked" product compared with the ether-linked analogue (Table 1). The higher thermal stability of the "clicked" polyacid could be explained with the formation of network through intermolecular electrostatic interactions between the sulfonic acid groups and triazole rings. Similar improved thermal behavior has been observed for ionically crosslinked polymer membranes.[29]

The aim of developing those highly efficient synthetic routes for the preparation of oppositely charged copolymers was to use them as building blocks for ionically crosslinked acid-base proton conducting blend membranes. It was expected that the blend membranes will show improved mechanical properties compared with the sulfonated copolymers alone. Although the blend membranes obtained were less brittle than those from pure polymeric sulfonic acids, it was still not possible to investigate their proton conductivity.

TABLE 1 Thermal Properties of the Functional Copolymers

Polymer	T_g (°C)	$T_{d5\%}$ (°C)	$T_{d90\%}$ (°C)
PS-*ran*-PBS	94	318	434
PS-*ran*-PHS	113	376	438
PS-*ran*-PAS	88	410	458
PS-*ran*-PDMAESCl	89	364	452
PS-*ran*-PAPSCl	104	362	451
PS-*ran*-IPSPSCl (salt)	163	323	439
PS-*ran*-PSPSCl (acid)	175	288	448
PS-*ran*-PAPS	93	374	449
PS-*ran*-PSPS (salt)	151	384	436
PS-*ran*-PSPS (acid)	121	260	447

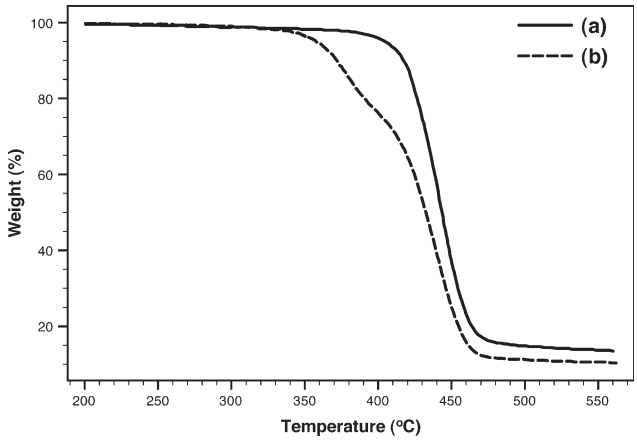


FIGURE 3 TGA curves for (a) alkyne-functionalized precursor PS-*ran*-PAS and (b) functionalized with tertiary amine pendant groups copolymer PS-*ran*-PDMAESCl.

CONCLUSIONS

Polystyrene-based random copolymers with stoichiometrically balanced acidic or basic pendant groups were obtained through a modification of the same template polymer backbone. The oppositely charged aliphatic groups were attached in quantitative manner applying "click" chemistry or conventional etherification reactions. The thermal properties evaluation revealed that the glass transition temperature and the thermal stability of the copolymers are strongly influenced by the presence of different pendant groups as well as by the method of modification.

The financial support from the Danish Council for Strategic Research through contract no. 2104-08-0016 is gratefully acknowledged.

REFERENCES AND NOTES

1 Thünemann, A.; Müller, M.; Dautzenberg, H.; Joanny, J.-F.; Löwen, H. Adv Polym Sci 2004, 166, 113–171.

2 Lam, J.; Ma, Y.; Armes, S.; Lewis, A.; Baldwin, T.; Stolnik, S. J Controlled Release 2004, 100, 293–312.

3 Funhoff, A.; Monge, S.; Teeuwen, R.; Koning, G.; Schuurmans-Nieuwenbroek, N.; Crommelin, D.; Haddleton, D.; Hennink, W.; van Nostrum, C. J Controlled Release 2005, 102, 711–724.

4 Dufresne, M.-H.; Leroux, J.-C. Pharm Res 2004, 21, 160–169.

5 Dumitriu, S.; Chornet, E. Biotechnol Prog 1997, 13, 539–545.

6 Chu, C.; Kumagai, H.; Nakamura, K. J Appl Polym Sci 1996, 60, 1041–1047.

7 Iwatsubo, T.; Kusumocahyo, S. P.; Shinbo, T. J Appl Polym Sci 2002, 86, 265–271.

8 Wang, Y.; Gao, J. Y.; Dubin, P. L. Biotechnol Prog 1996, 12, 356–362.

9 Lutkenhaus, J.; Hammond, P. Soft Matter 2007, 3, 804–816.

10 Kerres, J.; Ulrich, A.; Meier, F.; Haring, T. Solid State Ionics 1999, 125, 243–249.

11 Kerres, J. Fuel Cells 2005, 5, 230–247.

12 Harada, A.; Kataoka, K. Macromolecules 1995, 28, 5294–5299.

13 Koide, A.; Kishimura, A.; Osada, K.; Jang, W.-D.; Yamasaki, Y.; Kataoka, K. J Am Chem Soc 2006, 128, 5988–5989.

14 Schrage, S.; Sigel, R.; Schlaad, H. Macromolecules 2003, 36, 1417–1420.

15 Yusa, S.; Yokoyama, Y.; Morishima, Y. Macromolecules 2009, 42, 376–383.

16 Dimitrov, I.; Jankova, K.; Hvilsted, S. J Polym Sci Part A: Polym Chem 2008, 46, 7827–7834.

17 Daugaard, A.; Hvilsted, S. Macromol Rapid Commun 2008, 29, 1119–1125.

18 Rostovtsev, V.; Green, L.; Fokin, V.; Sharpless, K.; Angew Chem Int Ed Engl 2002, 41, 2596–2599.

19 Tornoe, C.; Christensen, C.; Meldal, M. J Org Chem 2002, 67, 3057–3064.

20 Takizawa, K.; Nulwala, H.; Thibault, R.; Lowenhielm, P.; Yoshinaga, K.; Wooley, K.; Hawker, C. J Polym Sci Part A: Polym Chem 2008, 46, 2897–2912.

21 Damiron, D.; Desorme, M.; Ostaci, R.-V.; Al Akhrass, S.; Hamaide, T.; Drockenmuller, E. J Polym Sci Part A: Polym Chem 2009, 47, 3803–3813.

22 Vestberg, R.; Piekarski, A.; Pressly, E.; Van Berkel, K.; Malkoch, M.; Gerbac, J.; Ueno, N.; Hawker, C. J Polym Sci Part A: Polym Chem 2009, 47, 1237–1258.

23 Thomsen, A.; Malmström, E.; Hvilsted, S. J Polym Sci Part A: Polym Chem 2006, 44, 6360–6377.

24 Carboni, B.; Benalil, A.; Vaultier, M. J Org Chem 1993, 58, 3736–3741.

25 Ryu, E.; Zhao, Y. Org Lett 2005, 7, 1035–1037.

26 Pang, J.; Zhang, H.; Li, X.; Jiang, Z. Macromolecules 2007, 40, 9435–9442.

27 Gao, Y.; Robertson, G.; Kim, D.-S.; Guiver, M.; Mikhailenko, S.; Li, X.; Kaliaguine, S. Macromolecules 2007, 40, 1512–1520.

28 Xue, L.; Wan, L.; Hu, Y.; Shen, X.; Huang, F.; Du, L. Thermochim Acta 2006, 448, 147–153.

29 Lee, J.; Kerres, J. J Membr Sci 2007, 294, 75–83.