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Synthesis and Characterization of Block-Graft Copolymers [poly(epichlorohydrin-*b*-styrene)-*g*-poly(methyl methacrylate)] by Combination of Activated Monomer Polymerization, NMP and ATRP

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Summary

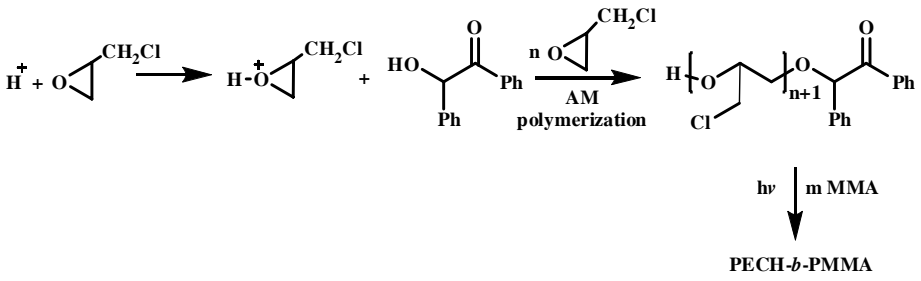
Synthesis of block-graft copolymers, namely poly(epichlorohydrin-*b*-styrene)-*g*-poly(methyl methacrylate) (PECH-*b*-St)-*g*-PMMA) by combination of Activated Monomer (AM), Nitroxide Mediated Polymerization (NMP) and Atom Transfer Radical Polymerization (ATRP) methods was described. For this purpose, first epichlorohydrin (ECH) was polymerized by using BF_3·THF complex in the presence of 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyl-1-oxy (HTEMPO) via AM mechanism. The resulting stable radical terminated polymer was subsequently used as a counter radical in the NMP of styrene (St) initiated by benzoyl peroxide to yield block copolymers of ECH and St. Finally, the ATRP of methyl methacrylate (MMA) by using chloromethyl groups of the PECH segment as initiating sites resulted in the formation of (PECH-*b*-St)-*g*-PMMA). The structures of the intermediate polymers at various stages were characterized by ^{1}H-NMR spectral investigations. The thermal behavior and surface morphology of the copolymers were also investigated by DSC and AFM measurements.

Introduction

The synthesis of novel polymeric materials with improved properties and performance has become an attractive field of polymer science. Block and graft copolymers that provide specific combinations of physical properties are the most suitable materials for various purposes [1]. Controlled radical polymerization became an established method to prepare new complex architectures of polymers such as block, graft, star and functional polymers with controlled molecular weight and molecular weight distribution. Nitroxide Mediated Polymerization (or stable radical mediated polymerization) (NMP) [2], Atom Transfer Radical Polymerization (ATRP) [3], and

Reversible Addition Fragmentation Transfer (RAFT) [4] processes are well known techniques in this field. NMP can be realized through reversible deactivation of growing radicals by stable radical such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). ATRP involves reversible homolytic cleavage of a carbon-halogen bond by a redox reaction between an organic halide (R-X) and a transition metal, such as copper (I) salts.

Traditionally, block copolymers have been synthesized via the sequential living polymerization of different monomers. However, the limited number of suitable monomers places restrictions on the number of copolymers that can be synthesized by this method [5]. By contrast, transformation reactions [6-8] have provided additional routes for the production of a wide range of block and graft copolymers, including varied type of monomers. The reactive end groups present on precursor polymers allow their utilization as platforms from which monomers can be polymerized or as linking groups which may react with other preformed polymer. For example, activated monomer (AM) polymerization [9-11] was used to produce polymers with terminal functional benzoin groups (Scheme 1.) [12-14]. Such photoactive polymers can be used in the preparation of block copolymers of monomers with different chemical nature.



Scheme 1

In this study, we report the preparation of block-graft copolymers, namely poly(epichlorohydrin-*b*-styrene)-*g*-poly(methyl methacrylate) by combination of AM, NMP and ATRP methods.

Experimental

Materials

4-Hydroxy-2,2,6,6-tetramethyl-1-piperidinyl-1-oxy (HTEMPO) (Aldrich), benzoyl peroxide (BPO) (Aldrich), L-(+)-ascorbic acid (Aldrich), and copper (I) chloride ($CuCl_1$) (Aldrich) were used without further purification. Epichlorohydrin (ECH) was purified by fractional distilliation. The middle fraction (80 vol %) was collected (bp= 116°C at 760 mmHg. n^{20}_D= 1.4380, purity 99.5 % by GLC). Methyl methacrylate (MMA) (Aldrich) and styrene (St) (Aldrich) were purified by the conventional method and distilled at reduced pressure over calcium hydride (CaH2)

before use. *N,N,N,N,N*-pentamethyldiethylenetriamine (PMDETA; Aldrich) was distilled over NaOH before use.

Activated Monomer Polymerization of ECH

HTEMPO (1.28g., 0.0074 mol) was dissolved in 2 mL of benzene in 2-necked flask equipped with neutral gas (argon) inlet, 0.365 g (0,0026 mol) of BF_3·THF complex was added and 5.2 g (0.0562 mol) of ECH was added drop wise to reaction mixture stirred by magnetic bar during 4h at room temperature. Reaction mixture was kept at room temperature for 5 days. It was then diluted with 5 mL of benzene and 1 g of solid CaO was added to neutralize the catalyst. After filtration volatiles were evaporated on vacuum line. 6.4 g of dark-yellow, viscous liquid was obtained.

Block Copolymerization by NMP

A 5 ml round bottom-flask equipped with magnetic stirrer and a lateral neck with tap were used. The system was vacuumed and back-filled with dry nitrogen several times. PECH-TEMPO with n = 7.3, (Mn_{GPC} = 840, M_w/M_n = 1.32), benzoyl peroxide (BPO) and styrene (St) were introduced under inert atmosphere. The polymerization was carried out at first for 3.5 h at 95°C, and then continued for another 19 h at 125°C. The mixture was diluted with THF and poured into ten-fold excess of methanol. The solid was collected after filtration and dried at room temperature in a vacuum overnight.

Graft Copolymerization by ATRP

A 5 ml round bottom-flask equipped with magnetic stirrer and a lateral neck with tap was used. The system was vacuumed and back-filled with dry nitrogen several times. Catalyst ($CuCl_1$), ligand (PMDETA), initiator (PECH-*b*-PSt) and monomer (MMA) were introduced under inert atmosphere. The flask was placed in an oil bath warmed at 90°C and stirred at that temperature. After a given time, the mixture was diluted with THF and poured into ten-fold excess of methanol. The solid was collected after filtration and drying at room temperature in a vacuum overnight.

Cleavage of the Block Copolymers

60 mg of the graft polymer and 6mg of L-(+)-ascorbic acid were put into an ampoule, dissolved in 5 mL dioxane and purged with nitrogen for 30 min. The ampoule was closed gastight and heated to 125°C for 24 h. After reaction th mixtures precipitated by pouring them into the ten-fold excess of cyclohexane. Cyclohexane is a good solvent for PSt, a nonsolvent for PMMA. The resulting insoluble and soluble fractions were analyzed by GPC.

Analysis

^{1}H-NMR spectra were recorded on a Bruker 250 MHz spectrometer using $CDCl_3$ as solvent and tetramethylsilane as the internal standard. Molecular weights were determined by gel-permeation chromatography (GPC) instrument equipped with Waters styragel column (HR series 2, 3and 5E) with THF as the eluent at a flow rate

of 0,3 ml/min and a Waters 410 Differential Refractometer detector and using polystyrene standards. Differential scanning calorimetry (DSC) was performed on Perkin-Elmer Diamond DSC with a heating rate of 10°C/min under nitrogen flow calibrated by indium. MALDI TOF spectra were recorded with a Voyager Elite MALDI TOF spectrometer using dihydroxybenzoic acid as a matrix and nitrogen laser desorption at 337 nm. Sodium iodide was used as cationating agent. Preparation of samples for AFM, Solutions of graft copolymers were prepared in toluene at a concentration of 5 mg/mL. Films were spin-coated at 2000 rpm for 1 min from these solutions on oxidized silicon substrates. Spin-coated films were kept in vacuum oven at low temperatures for solvent evaporation.

Results and Discussion

Our strategy for the synthesis of block-graft copolymers by combining controlled radical polymerization methods with AM polymerization was first to obtain well-defined polyepichlorohydrin (PECH), which contain terminal TEMPO and pendant chlorine moieties that give the possibility for further modification. In the next step, the resulting polymer could serve as a polymeric radical in the NMP of styrene with benzoyl peroxide (BPO) to give the corresponding block copolymer quantitatively. In the final step, block copolymer containing chlorine groups in one segment was used as a backbone to explore the possibility of using ATRP in the preparation of block-graft copolymer by the "grafting from" method.

ECH was polymerized using 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyl-1-oxy (HTEMPO) as a hydroxyl-containing compound according to following reactions (Scheme 2). Generally, epichlorohydrin (ECH) polymerizes smoothly in the presence of alcohols or diols by AM mechanism [11]. With HTEMPO as initiator polymerization was slow even in the presence of high concentration of catalyst (BF_3 complex). In spite of that practically complete conversion of ECH could be reached although it required relatively long reaction times.

As described in the experimental part, polymerization of ECH with HTEMPO was conducted at $[ECH]_0/[HTEMPO]_0$ ratio equal to 7.6, thus (at complete conversion) one can expect formation of oligomer with $DP_n = 7.6$. GPC analysis of the product leads to the value of $M_n = 840$ (polystyrene calibration). Considering that the molecular weight of the end-group derived from HTEMPO is equal to 172, the molecular weight of PECH chain is close to 670 that corresponds to $DP_n = 7.3$ which is very close to the theoretical value.

MALDI TOF analysis confirm that the product is essentially the TEMPO terminated PECH. Although, other macromolecules may be present in small but detectable amounts (these may be cyclic macromolecules or TEMPO terminated macromolecules containing THF unit(s) from catalyst).

MALDI TOF spectrum is shown in Figure 1 (to show the details only the enlarged fragment of the spectrum corresponding to DP = 5 and 6 is presented, the same series appear in other fragments of the spectrum).

In the inlet the expanded spectrum of oligomer with DP = 5 (with Na^+) is compared with the simulated one, the good agreement confirms that the assignments are correct. Thus the results of GPC and MALDI TOF analysis confirm that the product is indeed the TEMPO terminated PECH.

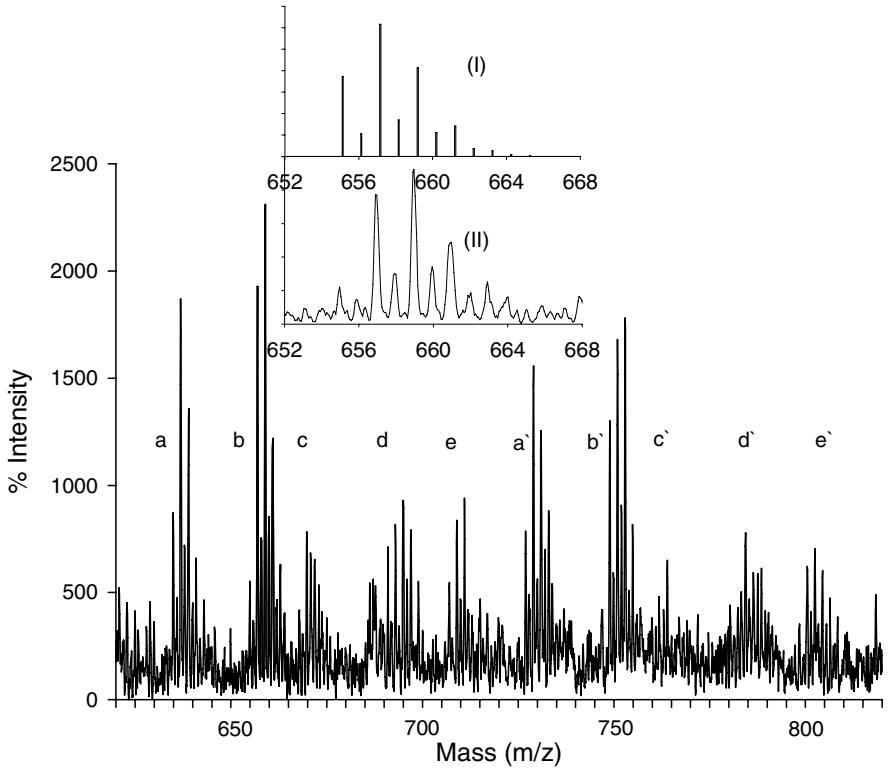
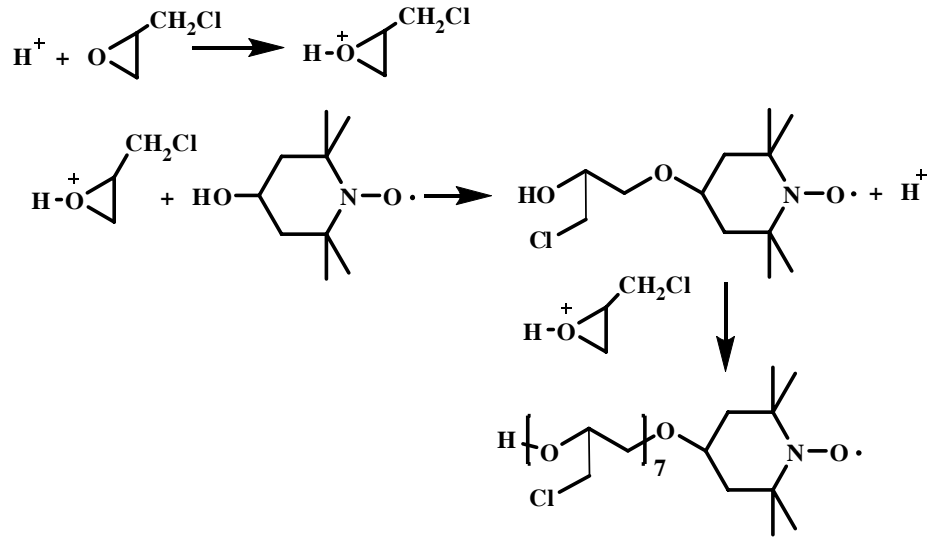


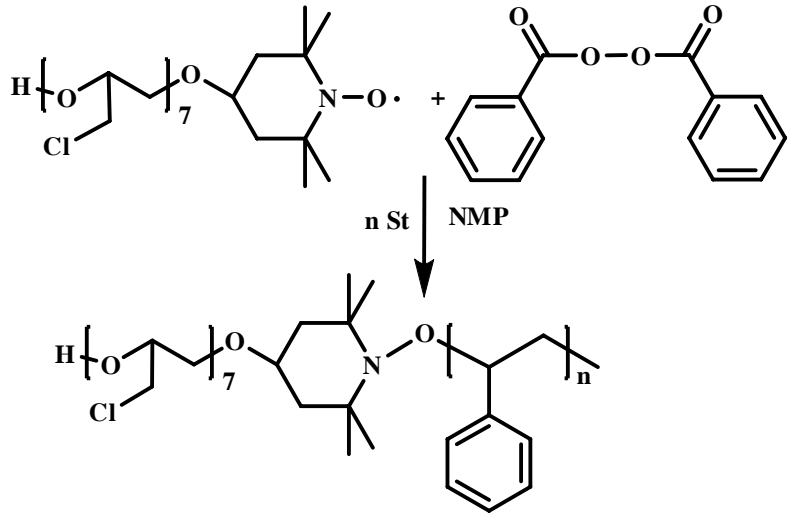
Figure 1. MALDI TOF spectrum of TEMPO terminated PECH ((fragment of the spectrum corresponding to m/z values between 600 and 800 shown).
Series a: TEMPO terminated PECH (n=5) + H^+ (m/z = 635.5) or TEMPO terminated PECH (n=4) containing one THF unit + Na (m/z = 637) , series b: TEMPO terminated PECH (n = 5) + Na^+ (657,5), series c: TEMPO terminated PECH (n = 5) + K^+ (m/z = 674) or cyclic PECH (n = 7) + Na^+ (m/z = 670.5), d: unidentified, e: TEMPO terminated PECH (n = 4) containing two THF units + Na^+ (m/z = 709). Signals marked with superscript, correspond to the same series containing one more ECH unit. In the inlet the observed isotope distribution (resulting mainly from the presence of ^{35}Cl and ^{37}Cl atoms) for TEMPO terminated PECH with n = 5 (+ Na^+) is compared with a calculated one. Not all of the signals can be unequivocally assigned because of the possible overlapping of signals and their complex nature. The complex nature of signals results from the presence of several chlorine atoms in macromolecules (natural abundance: 75% of ^{35}Cl and 25% of ^{37}Cl). As shown in Figure Caption most signals can be assigned to TEMPO terminated PECH macromolecules.

The incorporation of the stable radical was evidenced by ^{1}H-NMR measurement of the product treated with phenylhydrazine which reduces TEMPO moiety into the corresponding hydroxylamine. In ^{1}H-NMR spectra, the group of signals 3.5-3.8 ppm, corresponding to CH_2-O, CH_2-C1, and CH protons of PECH chain appears, together with a signals in the range 1.2 and 1,6-1.9 ppm, corresponding CH_3 and CH_2 groups of the terminal TEMPO moiety (Figure 2A).
The resulting PECH could serve as a polymeric counter radical [15, 16] in the radical polymerization of styrene with benzoyl peroxide (BPO) to give the corresponding block copolymer quantitatively (Scheme 3). The results are summarized in Table 1.



Scheme 2

As can be seen, the concentration and polymerization time affect the length of the second segment as well as the polydispersity. Considering the initial polydispersity of the precursor PECH (Mw/Mn=1.32), block copolymers with reasonably low molecular weight distributions (Mw/Mn=1.52) may be obtained at selected conditions. The ^{1}H-NMR spectrum of the block copolymer (Figure 2B) displays signals at 1.2-2.0 (CH_2 and CH of St segments), 3.55-3.8 (CH_2-O, CH_2-C1, and CH protons of ECH segments), and 6.5-7.3 ppm (C_6H_5 of St segments). The molecular weights increased after the polymerization, and the polydispersities were slightly broadened (Figure 3B).

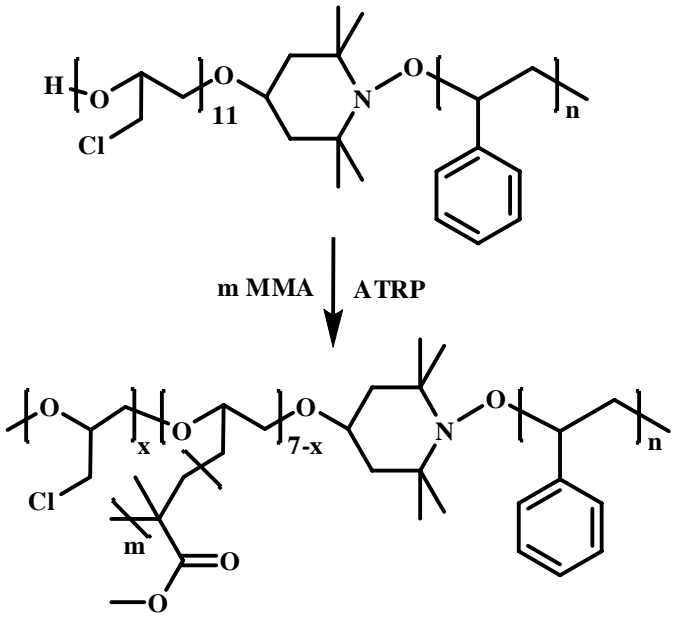


Scheme 3

Table 1. Synthesis of PECH-*b*-PSt block copolymer by Nitroxide Mediated Polymerization

[M]/[I] /[PECH][a]	Time[b] (h)	Con.[c] (%)	Mn_{GPC}[d]	Mn_{NMR}[e]	Mw/Mn[d]	Composition ECH[e] (%)	Composition St[e] (%)	Block copolymer
65/1/1.3	19	65	24700	20400	2.36	4.1	95.9	B-1
130/1/1.3	19	45	23000	19600	1.91	4.3	95.7	B-2
130/1/1.3	15	34	24500	20300	1.52	4.1	95.9	B-3
65/1/1.3	10	58	14000	13100	1.75	6.4	93.6	B-4

[a][M]/[I]/[PEC] = 0.00875/0.00135/0.000175 M
[b]Reaction temperature = first 3.5 hours at 95°C and remaining time 125°C
[c]Conversion of PSt
[d]Estimated by GPC based on polystyrene standards
[e]Estimated by ^{1}H-NMR spectroscopy



Scheme 4

Percec and Bicak groups used allylic defects of the polyvinyl chloride to synthesize graft copolymers by ATRP [17, 18]. Recently, Cakmak et al. synthesized PECH-*g*-PSt and PECH-*g*-PMMA graft copolymers by combination of cationic and atom transfer radical polymerization [19]. In our work, chloromethyl groups of the PECH segment were used as the initiating sites for the final ATRP process. The formation of block-graft copolymer was evidenced by ^{1}H-NMR and GPC analyses. As can be seen from the ^{1}H-NMR spectrum of the polymer recorded after the ATRP step, the peak appearing at about 3.6 ppm corresponding to O-CH_3 protons shows the presence of grafted MMA units (Figure 2C). Furthermore, shifting of the initial peak of the precursor block copolymer to higher elution volumes indicates that block-graft copolymer was successfully obtained (Figure 3C). The results are summarized in Table 2. The grafting density is defined as the number of grafted polymer chains per

number of backbone chains. Using block copolymers having short backbone increase the grafting density of final block-graft copolymers.

Table 2. Synthesis of [PECH-*b*-PSt]-*g*-PMMA block-graft copolymer by Atom Transfer Radical Polymerization[a]

Prepolym	Con.[b] %	Mn_{GPC}[c]	Mn_{NMR}[d]	Mw/ Mn[c]	Grafting density[e]	Composition ECH[d] (%)	Composition St[d] (%)	Composition MMA[d] (%)	Final
B-2	44	51400	30450	1.97	0.6	2.7	64.3	33	G1
B-1	64	78500	55800	2.65	1.9	1.5	36.6	61.9	G2
B-3	68	83000	59100	2.37	2.1	1.4	33.2	65.4	G3
B-4	57	75600	54000	2.50	3.5	1.5	24.3	74.2	G4

[a][M]/[Prepolymer]/[CuCl]/[Ligand] = 18/0,001/0,1/0,3 M, 2 h, 90°C.
[b]Conversion of PMMA.
[c]Estimated by GPC based on polystyrene standards.
[d]Estimated by ^{1}H-NMR spectroscopy.
[e]Grafting density = DPsc(degree of polymerization of side chain)/DPbb(degree of polymerization of backbone) calculated from ^{1}H-NMR analysis [20].

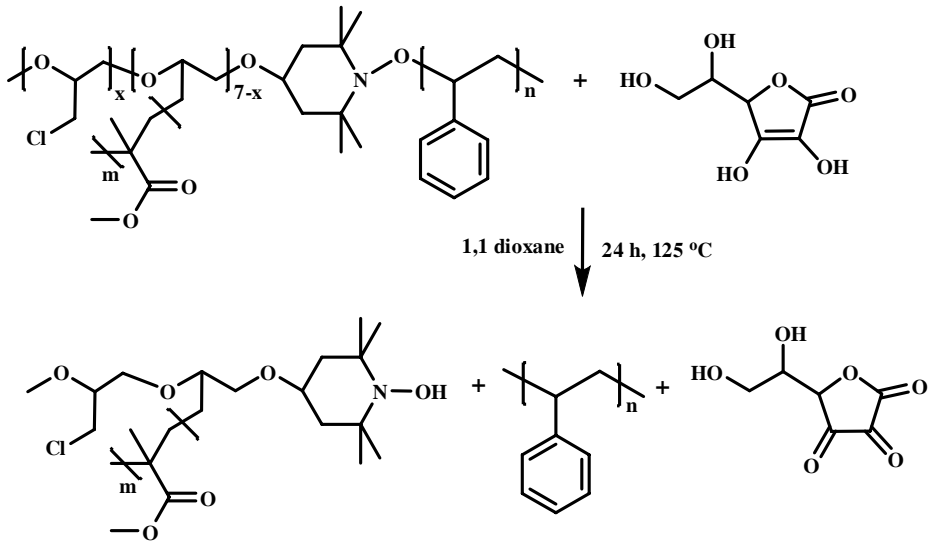
Ascorbic acid can easily reduce TEMPO to the corresponding PECH-*g*-PMMA graft copolymer and homo polystyrene by the reaction shown in Scheme 5 [21]. The GPC results of cleavage products were collected in Table 3. As can be seen the molecular weights decreased, and molecular weight distributions became narrower.

Table 3. Molecular weights and polydispersities of homopolymers and graft copolymers obtained after cleavage

Copolymers	Mn_{PSt}[a]	Mw/Mn_{PSt}[a]	$Mn_{PECH\text{-}g\text{-}PMMA}$[a]	$Mw/Mn_{PECH\text{-}g\text{-}PMMA}$[a]
G1	16800	1.38	32800	1.90
G2	20400	1.67	51600	1.96
G3	19100	1.45	65400	2.08
G4	15100	1.55	60400	2.22

[a]Estimated by GPC based on polystyrene standards.

Thermal behavior of these block copolymers was examined by differential scanning calorimetry (DSC) in the range of -50 to +150°C. Typical glass transition temperatures (T_gs) of the corresponding homopolymers; PECH, PSt and PMMA were reported to be -22, 100 and 120°C, respectively. In our work, TEMPO functionalized PECH showed at T_g -20°C. The DSC thermogram of the block copolymers exhibited two T_g*s* -5 and 93°C, which correspond to the PECH and PSt chains, respectively. Interestingly, the effect of the each segment on the T*g* of the other respective segment was noticeable. Such behavior was also observed for structurally similar block copolymers [22]. The T_g's of block-graft copolymers with PECH-*b*-PSt backbone and PMMA side chain segments have values of 102 and 122°C. T_g of PECH could not be detected due to very small ratio in the block-graft copolymer (~ % 1).



Scheme 5

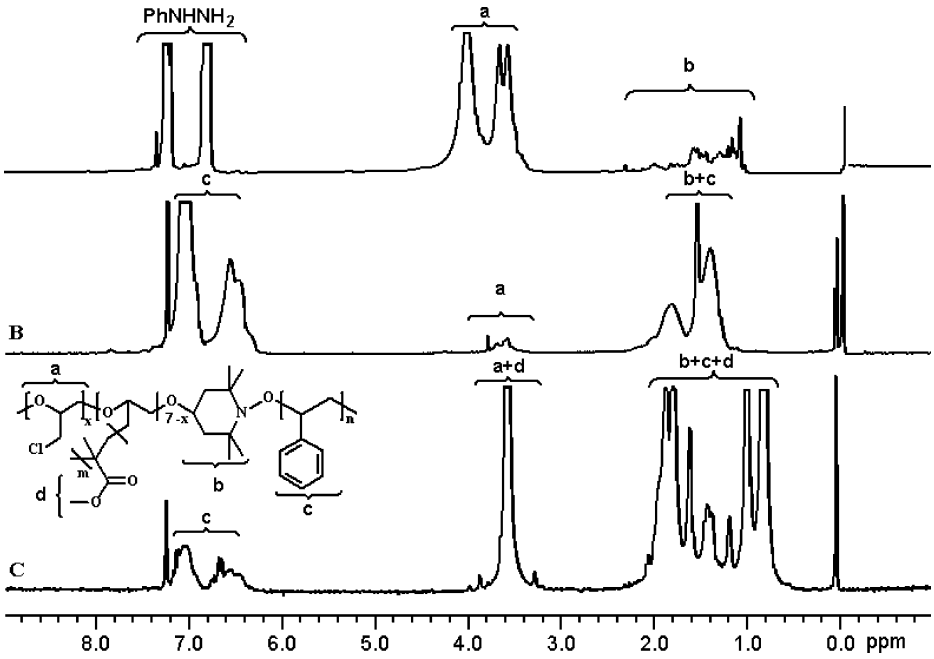


Figure 2. ^{1}H-NMR spectra of **A)** PECH in the presence of phenylhydrazine **B)** PECH-*b*-PSt **C)** [PECH-*b*-PSt]-*g*-PMMA.

The surface of the spin coated graft polymer films was very smooth (peak to peak roughness < 2 nm) as seen in the Atomic Force Microscopy (AFM) height image of Figure 4a. The corresponding AFM phase picture (Figure 4b) showed very clear phase contrast of the two different types of polymers. The bright regions were nearly

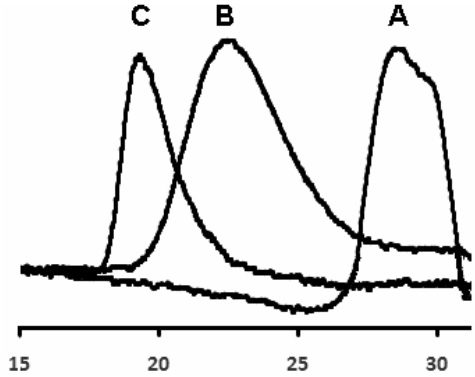


Figure 3. GPC traces of **A)** PECH **B)** PECH-*b*-PSt **C)** [PECH-*b*-PSt]-*g*-PMMA.

continuous throughout the surface with darker regions trapped between them. Both regions were mostly elongated with an average width of ~ 50 nm. These contrast undulations indicate immiscible polymers of different viscoelasticity on the surface. Although the molecular weight of PSt is less than that of PMMA, we attribute the brighter regions covering a larger area to the PSt block. The lower surface energy of PSt enhances the segregation of PSt block to the top surface. The darker regions correspond to the PMMA block.

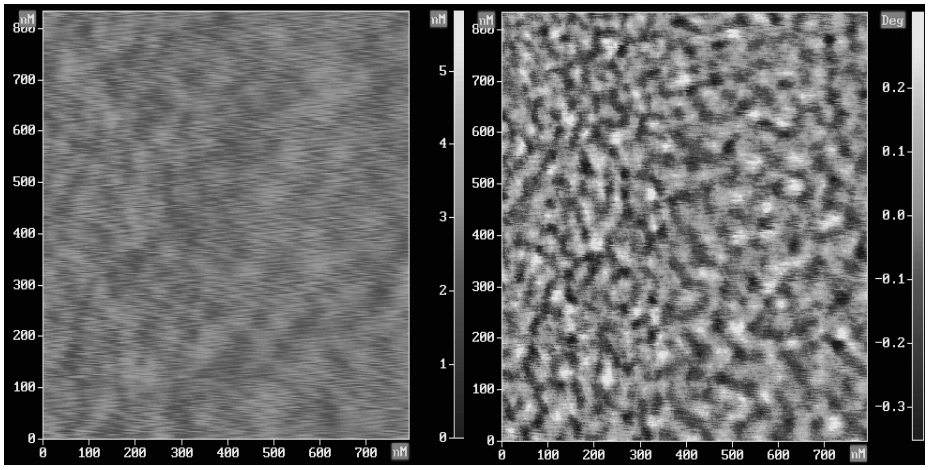


Figure 4. AFM height (a) and phase (b) pictures of graft polymer film.

Conclusions

PECH with end-chain and side-chain functionalities (e.g. TEMPO and chlorine, respectively) can be prepared by AM polymerization. The resulting polymer acts as a counter radical for NMP of St and in the subsequent step, as an initiator for the ATRP of MMA yielding block-graft copolymers.

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