

Amphiphilic Diblock Copolymers Poly(2-hydroxyethylmethacrylate)-*b*-(*N*-phenylmaleimide) and Poly(2-hydroxyethylmethacrylate)-*b*-(styrene) Using the Macroinitiator Poly(HEMA)-Cl by ATRP: Preparation, Characterization, and Thermal Properties

Guadalupe del C. Pizarro,¹ Oscar G. Marambio,¹ Manuel Jeria-Orell,¹ Mario E. Flores,¹ Bernabé L. Rivas²

¹Department of Chemistry, Technological Metropolitan University, Santiago, Chile

²Polymer Department, Faculty of Chemistry, University of Concepción, Casilla, Concepción, Chile

Received 24 July 2009; accepted 27 February 2010

DOI 10.1002/app.32353

Published online 15 July 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In recent years, much attention has been given to the development of specialty polymers from useful materials. In this context, amphiphilic block copolymers were prepared by atom transfer radical polymerization (ATRP) of *N*-phenylmaleimide (*N*-PhMI) or styrene using a poly(2-hydroxyethylmethacrylate)-Cl macroinitiator/CuBr/bipyridine initiating system. The macroinitiator P(HEMA)-Cl was directly prepared in toluene by reverse ATRP using BPO/FeCl₃·6 H₂O/PPH₃ as initiating system. The microstructure of the block copolymers were characterized using FTIR, ¹H-NMR, ¹³C-NMR spectroscopic techniques and scanning electron microscopy (SEM). The thermal behavior was studied by differential scanning calorimetry (DSC), and thermogravimetry (TG). The theoretical number average molecular weight ($M_{n,th}$) was calculated from the feed capacity. The microphotographs of the film's surfaces show that the film's top

surfaces were generally smooth. The TDT of the block copolymer P(HEMA)₈₀-*b*-P(*N*-PhMI)₂₀ and P(HEMA)₉₀-*b*-P(St)₁₀ of about 290°C was also lower than that found for the macroinitiator poly(HEMA)-Cl. The block copolymers exhibited only one T_g before thermal decomposition, which could be attributed to the low molar content of the *N*-PhMI or St blocks respectively. This result also indicates that the phase behavior of the copolymers is predominately determined by the HEMA block. The curves reveal that the polymers show phase transition behavior of amorphous polymers. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3649–3657, 2010

Key words: controlled radical polymerization (ATRP); diblock copolymers; amphiphilic block copolymers; thermal behavior; transition glass temperature (T_g)

INTRODUCTION

To adequately face the new challenges generated by the specific necessities associated with technological advance resulting from interaction between diverse areas, the high tech industry has progressively increased its demand for new materials in the last few decades. In this context, block copolymers are formed by the covalent union of two or more polymer chains, which generally are thermodynamically incompatible, giving rise to a great variety of microstructures as well as solid state in dissolution. These

materials are very attractive for use in the synthesis of functional nanostructures because their length as well as spatial organization can be controlled through block copolymer morphology.^{1,2} In the last decade, important advances in radical polymerization reactions have led to the development of synthesis methods that eliminate (or diminish to a large extent) undesirable chain termination and transfer reactions.

For a controlled radical polymerization, three methods are generally applied. The first is the Nitroxide-Mediated Radical Polymerization (NMP).^{3–5} The second corresponds to transition metal complexes, such as CuX/bipyridine and other metal complexes with Ru, Fe, Ni, Rh, and Pd, which through a reversible catalytic action, results in Atom Transfer Radical Polymerization (ATRP).^{6–8} The third technique corresponds to Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization.^{9–12}

Of the three new synthesis methods mentioned, the ATRP technique has been used with monomers derived from acrylic acid at room temperature in the

Correspondence to: G. D. C. Pizarro (gpizarro@omega.UTEM.cl).

Contract grant sponsor: Dirección de Investigación de la Universidad Tecnológica Metropolitana Project; contract grant number: 294/2007.

Contract grant sponsor: Deutsche Akademische Austauschdienst (DAAD), CIPA.

presence of different lateral groups, which are susceptible to ionic or radical reactions. Matyjaszewski et al.¹³ reported the atom transfer radical polymerization of 2-hydroxyethylmethacrylate. ATRP has been used to directly prepare linear PHEMA of controlled molecular weight and low polydispersity. Polymerization reaction condition adjustments included the use of a mixed solvent system, consisting of methyl ethyl ketone and 1-propanol lowering the temperature to 50°C or less and using an alkyl bromide initiator with a copper chloride catalyst. Armes and coworkers¹⁴ reported the stimulus-responsive water-soluble polymers based on 2-hydroxyethylmethacrylate. The homopolymerization and block/statistical copolymerization of 2-hydroxyethylmethacrylate using ATRP in methanol at 20°C have been investigated. Meizhen et al.¹⁵ reported a study of controlled radical synthesis of well-defined polystyrene and block copolymerization with 2-hydroxyethylmethacrylate or 2-hydroxyethylacrylate, respectively using styrene macroinitiator initiated by NMP methods, using a nitroxide such as TEMPO as initiator system. However, TEMPO-based unimolecular initiators present certain problems, such as the necessity to use high polymerization temperatures (125–145°C), long reaction times (24–72 h), and incompatibility with many important monomer series.

In this context, the goal of our work is to evaluate the ability of a controlled radical polymerization of 2-hydroxyethylmethacrylate as macroinitiator (first block) initiated by the reverse ATRP method. Specifically, we present the kinetic study of the homogeneous ATRP of HEMA and report the polymerization rate's dependence on temperature. The polymer was directly prepared in toluene without protecting group chemistry to study the possibility of block copolymer formation with *N*-PhMI and styrene initiated by the ATRP method. The microstructure of the amphiphilic block copolymers were characterized using FTIR, ¹H-NMR, ¹³C-NMR spectroscopy, and scanning electron microscopy (SEM). The thermal behavior was studied by differential scanning calorimetry (DSC) and thermogravimetry (TG).

EXPERIMENTAL

Materials

Styrene (St): Commercial monomer (purchased from the Sigma-Aldrich chemicals, CHEMIE GmbH, Germany) was distilled under pressure before being utilized. 2-hydroxyethylmethacrylate (HEMA) (purchased from the Merck-Schuchardt OHG chemicals, Germany) was purified by distillation under reduced pressure. Benzoyl peroxide (BPO), iron(III) chloride hexahydrate (FeCl₃ · 6H₂O), triphenylphosphine (PPh₃), CuBr (copper(I) bromide), *N,N*-bipyridine (Bpy) reagents were purchased from Aldrich chemi-

cals, CHEMIE GmbH, and Merck-Schuchardt, Germany.

Synthesis of monomer derived from maleimide

N-phenylmaleimide (*N*-PhMI) was synthesized from maleic anhydride and aniline (purchased from the Sigma-Aldrich chemicals, CHEMIE GmbH, Germany) in diethyl ether using the reported procedure.¹⁶ Aniline was purified by distillation under reduced pressure. *N*-PhMI was purified by crystallization from cyclohexane. The yield was 77%, m.p. 93–95°C. ¹H-NMR spectra (CDCl₃; δ ppm) showed the resonance signals at: 6.82 [2H, CH=CH from imide]; and 7.3–7.6 [5H, —CH aromatic protons from imide]. FTIR spectrum (KBr, cm⁻¹) exhibits the most characteristic absorption bands: at 3089.7 cm⁻¹ [ν(CH, CH₂)]; 1711.8 cm⁻¹ [ν(—C=O)]; 1391.7 cm⁻¹ [ν(N—C, imide ring); 759.5 and 690.4 cm⁻¹ [ν(aromatic ring)].

General procedure for synthesis of macroinitiator

The macroinitiator was obtained by using the BPO/FeCl₃·6H₂O/PPh₃ system applying the atom transfer radical polymerization (ATRP) reverse in solution (toluene) based on reported procedure.¹ In a typical polymerization experiment, batch polymerization of monomer HEMA (14.38 mmol) occurred in a polymerization flask using BPO/FeCl₃·6H₂O/PPh₃ as initiator in a molar ratio of 200 (monomer) : 1 : 4 : 6. A mixture of 17.93 mg BPO (0.072 mmol), 77.86 mg FeCl₃·6H₂O, (0.288 mmol), and 113.3 mg PPh₃ (0.432 mmol) were placed in the polymerization flask. Three freezing-pump vacuum-thaw cycles (1.33 · 10⁻⁴ kPa) were applied to remove oxygen. Subsequently, 2 mL of HEMA (14.77 mmol) were added to the polymerization flask under a nitrogen atmosphere, and then it was placed in an oil bath at different temperatures (70, 80, and 90°C) (Table I). Throughout this period, the originally red translucent polymeric solution turned dark and opaque. After a certain reaction time, cooling with liquid nitrogen was applied to stop polymerization. The resulting polymer was precipitated in methanol, and purified by redissolution in methanol, and then dried at 60°C under vacuum to a constant weight. The obtained product was P(HEMA)-Cl. Yield (%) and theoretical number average molecular weight (*M_n*th) are presented in Table I.

General procedure for synthesis of diblock copolymer using PHEMA-Cl /CuBr /BPy, based on published procedure¹⁵

First, 1218.1 mg of macroinitiator (9.37 mmol, considering the molar mass of HEMA) was added to a

TABLE I
Experimental Conditions by Reverse Atom Transfer Radical Polymerization (ATRP)
of P(HEMA)-Cl

Sample No	Time (h)	Conv (%)	Yield (%)	$M_{n,th}$ (g/mol)
1	8	70	50	18 423.7
2	16	76	58	20 735.9
3	24	90	65	23 687.6

Initiator system (HEMA)/BPO/FeCl₃·6H₂O/PPh₃, feed molar ratio of 200/1/4/6; different time of reaction, temperature Reaction: 80°C.

S: Solution (solvent: Toluene).

The theoretical number average molecular weight ($M_{n,th}$) was calculated from the feed capacity. $M_{n,th} = (M_m \times \text{conversion} \times [M]/[I]) + M_i$, where M_m and M_i are the molar masses of monomers and initiator (or macroinitiator), respectively, $[M]$ and $[I]$ are the concentration of monomer and initiator (or macroinitiator), respectively.

polymerization flask and dissolved in toluene. Subsequently, 1621 mg (or 974.5 mg) of the second *N*-PhMI (or St) monomers (9.37 mmol respectively) and 30.6 mg of ligand, BPy (0.188 mmol) were added. Then, the mixture was purged by three cooling cycles with liquid nitrogen. While stirring at 25°C for 20 min, 13.5 mg CuBr (0.094 mmol) was added to the system, and placed in an oil bath at the previously defined working temperature. After a previously defined reaction time, it was cooled with liquid nitrogen to stop the reaction and the polymerization flask was opened. The mixture was dissolved in DMF, and then this solution was passed through a silica column to purify and completely remove the catalyst before characterization. Finally, the block copolymer was dried under vacuum up to constant weight (Table II).

Kinetic studies of the polymerization

Monomer conversion was determined by ¹H-NMR spectroscopy and the spectra were recorded in solution (DMSO-*d*₆) at room temperature. The HEMA monomer was used as internal reference in the measurement (1 mL). A series of 4 poly(HEMA) was synthesized with different time intervals (8, 16, 24, and 32 h) and at 80, 90°C in solution (toluene). The monomer conversion was determined directly from

the crude product (monomer and polymer in the reaction flask). Samples taken with different time intervals were analyzed by ¹H-NMR spectroscopy, which is shown in Figure 1. The conversion was determined for comparison of the integration areas of the peaks, considering the disappearance of the signal of the double bond CH=CH between 5.5–6.2 ppm and the signals for OH– (at 4.8 ppm, integration for 1H) and CH₃– (between 0.8–1.0 ppm, integration for 3H) groups. The HEMA monomer and poly(HEMA) present both the functional groups OH– and –CH₃, and the values of the integrals must remain in a relation 1 : 3, but the integration of the double bond decreases as the monomer disappears and becomes to polymer. The conversion was determined in percentage considering the decreases of signal of the double bond between 5.5–6.2 ppm (indicating the consumption of HEMA) and assuming the integration of OH– and CH₃– functional groups respectively as a 100%.

Measurements

FTIR spectra were recorded by a Bruker Vector 22 (Bruker Optics GmbH, Ettlingen, Germany). The ¹H-NMR spectra were recorded in solution at room temperature with a Bruker AC 250 (Bruker, Karlsruhe, Germany) spectrometer using deuterated

TABLE II
Experimental Conditions by Atom Transfer Radical Polymerization (ATRP) of
P(HEMA)-*b*-P(*N*-PhMI) and P(HEMA)-*b*-P(St)

Sample no	Block copolymer formula	Temp. (°C)	Yield (%)	$M_{n,th}$ (g/mol)
4	P(HEMA)- <i>b</i> -P(<i>N</i> -PhMI)	90	50	30 684.5
5	P(HEMA)- <i>b</i> -P(<i>N</i> -PhMI)	100	35	27 327.6
6	P(HEMA)- <i>b</i> -P(<i>N</i> -PhMI)	110	28	27 186.0
7	P(HEMA)- <i>b</i> -P(St)	90	60	25 793.2
8	P(HEMA)- <i>b</i> -P(St)	100	46	25 370.0

N-PhMI or St and initiator system P(HEMA)-Cl/CuBr/Bpy in a feed molar ratio of 100 : 100/1/2, Solvent : Toluene, at different temperature and 8 h of reaction.

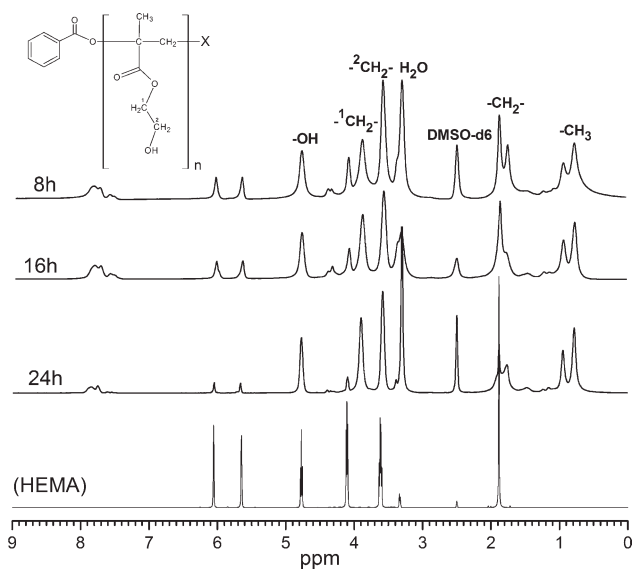


Figure 1 $^1\text{H-NMR}$ ($\text{DMSO-}d_6$) for poly(HEMA)-Cl at different polymerization time (a) 8 h, (b) 16 h, and (c) 24 h, at 80°C .

dimethylsulfoxide ($\text{DMSO-}d_6$, 99.8%), and $^{13}\text{C-NMR}$ spectroscopy. Elemental analyses were determined using a Carlo Erba 1106 analyzer (Italy). TG and DSC (Mettler Toledo Star System, Spain) thermograms were recorded under nitrogen atmosphere. A sample of $3\text{--}4 \pm 0.1$ mg was used in each experiment. Thermal stability studies were performed using a thermogravimetric analyzer (TG) at a heating rate of $10^\circ\text{C}/\text{min}$. DSC measurements were carried out with a Mettler Toledo Star System 822e to determine the copolymer's glass transition temperature (T_g). The T_g was measured with a heating rate of $10^\circ\text{C min}^{-1}$.

Copolymer morphology was examined by scanning electron microscopy (SEM) (Jeol, GSM-6380LV).

Block copolymer composition

The amphiphilic diblock copolymers $\text{P(HEMA)}_{80}\text{-}b\text{-P(N-PhMI)}_{20}$ and $\text{P(HEMA)}_{90}\text{-}c\text{-P(St)}_{10}$ can be denoted as copolymers 4 and 7, respectively (the subscript indicating the percentages of each block in the copolymer), (Table II). The composition percentage of the blocks was calculated by $^1\text{H-NMR}$ for

both copolymers systems; for $\text{P(HEMA)}_{80}\text{-}b\text{-P(N-PhMI)}_{20}$, the composition percentage additionally was calculated by elemental analyses according to the following equation (N content):

$$m_1 = \frac{M_2}{[(A_N/B) - \Delta M \times 10^{-2}]}$$

Where, M_1 is the molecular weight of N-PhMI ; A_N is the atom weight of N ; B is the content of N in the copolymers (%); $\Delta M = M_1 - M_2$. M_2 is the molecular weight of the HEMA, Table III.

Theoretical number average molecular weight

Theoretical number average molecular weight ($M_{n,th}$) was calculated from the feed capacity. $M_{n,th} = (M_m \times \text{conversion} \times [M]/[I]) + M_i$, where M_m and M_i are the molar masses of monomers and initiator (or macroinitiator), respectively, $[M]$ and $[I]$ are the concentration of monomer and initiator (or macroinitiator), respectively.

Preparation of the thin films

The morphology of the block copolymers was characterized by SEM on a thin film.

The amphiphilic block copolymer (10 mg polymer dry) is dissolved in chloroform/DMSO (for 2 days until forming a homogeneous solution, 0.5% w/v). The mixed solution was cast onto a 50-mm diameter plate and heated at 50°C for 2 days before thin film formation.

RESULTS AND DISCUSSION

Characterization of macroinitiator P(HEMA)-Cl

The characterization was carried out by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and FTIR spectroscopic techniques and SEM. Thermal analysis was performed using a thermogravimetric analyzer (TG) and differential scanning calorimetry (DSC). The initiator system used proved to be effective for the controlled radical polymerization of HEMA. As shown in Figure 2, the $\ln([M_0]/[M])$ plots versus time were linear, which confirm that the polymerization rate provides an

TABLE III
Copolymer Composition in Molar percentages (mol %) for Each Block Segments

No	Sample	Elemental analysis (%)			Copolymer composition	
		C	N	H	(EA)	$^1\text{H-NMR}$
4	$\text{P(HEMA)}\text{-}b\text{-P(N-PhMI)}$	55.2	1.63	6.52	80 : 20	77 : 23
5	$\text{P(HEMA)}\text{-}b\text{-P(N-PhMI)}$	56.8	1.48	8.51	84 : 16	76 : 24
6	$\text{P(HEMA)}\text{-}b\text{-P(N-PhMI)}$	55.4	1.02	8.64	90 : 10	86 : 14
7	$\text{P(HEMA)}\text{-}b\text{-P(St)}$	—	—	—	—	90 : 10
8	$\text{P(HEMA)}\text{-}b\text{-P(St)}$	—	—	—	—	92 : 8

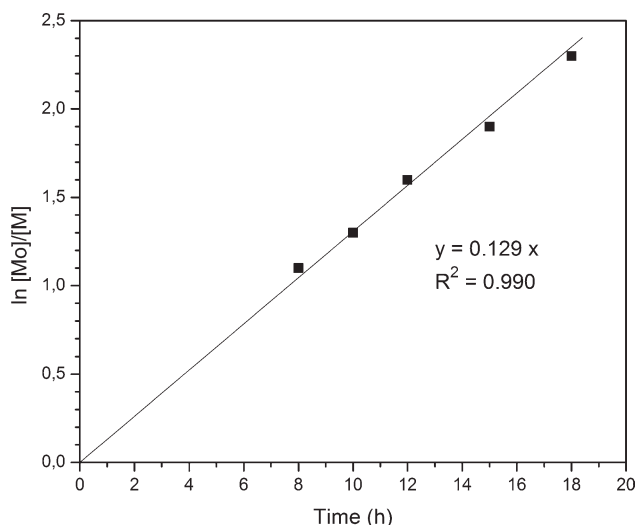


Figure 2 The $\ln([M_0]/[M])$ plots versus time.

excellent first-order relationship for homopolymer formation. The monomer conversion was determined by $^1\text{H-NMR}$ spectroscopy (Fig. 2). The macro-initiator without protecting group chemistry was soluble in dimethylsulfoxide and DMF. Due to the poor solubility of the polymer obtained, the experimental molecular weight by GPC could not be determined. The theoretical number average molecular weight ($M_{n,th}$) was calculated from the feed capacity. The polymerizations of HEMA exhibited an increase in molecular weight ($M_{n,th}$) in direct proportion to the ratio of the monomer consumed with respect to the initial initiator concentration.

The effect of the temperature on reverse ATRP was also studied by comparing polymerization at 70, 80, and 90°C for different reaction times (8, 16, and 24 h). In particular, the polymerization of HEMA at 90°C proceeded rather fast for the same reaction time, and achieved high conversions after 8–24 h, indicating an uncontrolled process, at least under these reaction conditions. In contrast at 70°C, the polymerization of HEMA occurred very slowly for the same reaction time and resulted in a low yield. Therefore, the temperature at 80°C was found to be the most efficient for the controlled radical polymerization of HEMA, where this temperature resulted in moderate conversion (65–90%) at 8, 16, 24, and 48 h of reaction. The reaction conditions and results are shown in Table I.

The $^1\text{H-NMR}$ spectra ($\text{DMSO-}d_6$; δ ppm) of P(HEMA)-Cl at 80°C and different reaction time are shown in Figure 2(a–c) and HEMA (2d). The signals of the main chain of PHEMA can be clearly observed at: 0.6–1.3 [3H, $-\text{CH}_3$]; 1.6–2.3 [2H, $-\text{CH}_2-$ from the backbone]; 2.5 and 3.3 solvent signals $\text{DMSO-}d_6$ and water, 3.4–4.2 [4H, $-\text{CH}_2-$ from HEMA]; 4.8 [1H, $-\text{OH}$].

$^{13}\text{C-NMR}$ ($\text{DMSO-}d_6$; δ ppm) spectrum exhibits the following signals at: 18 [$-\text{CH}_3$]; 40 solvent, 43 [$-\text{CH}_2$ from the backbone]; 60 and 68 [$-\text{CH}_2$ side chain from HEMA]; 180 [$-\text{C}=\text{O}$]. The FTIR spectrum (KBr, cm^{-1}) for P(HEMA)-Cl exhibits the most characteristic absorption bands: at 3424.6 cm^{-1} [$\nu(\text{OH})$]; at 2952.0 and 2885.5 cm^{-1} [$\nu(\text{CH}, \text{CH}_2)$]; at 1719.5 cm^{-1} [$\nu(-\text{C}=\text{O}, \text{ester})$] [Fig. 3(a)].

Characterization of amphiphilic block copolymers by ATRP P(HEMA)-*b*-P(N-PhMI) using P(HEMA)-Cl/CuBr/bpy

The microstructure of the amphiphilic block copolymers obtained by P(HEMA)-Cl/CuBr/Bpy initiating system was characterized using FTIR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ spectroscopy, and SEM. Thermal characterization was performed using differential scanning calorimetry (DSC) and thermogravimetry (TG). The temperature effect on ATRP was also investigated comparing the polymerization at 90, 100, and 110°C at 8 h of reaction. The experimental copolymerization conditions and results are shown in Table II. In particular, the copolymerization reaction at 90°C proceeded rather fast for the same reaction time in comparison with the

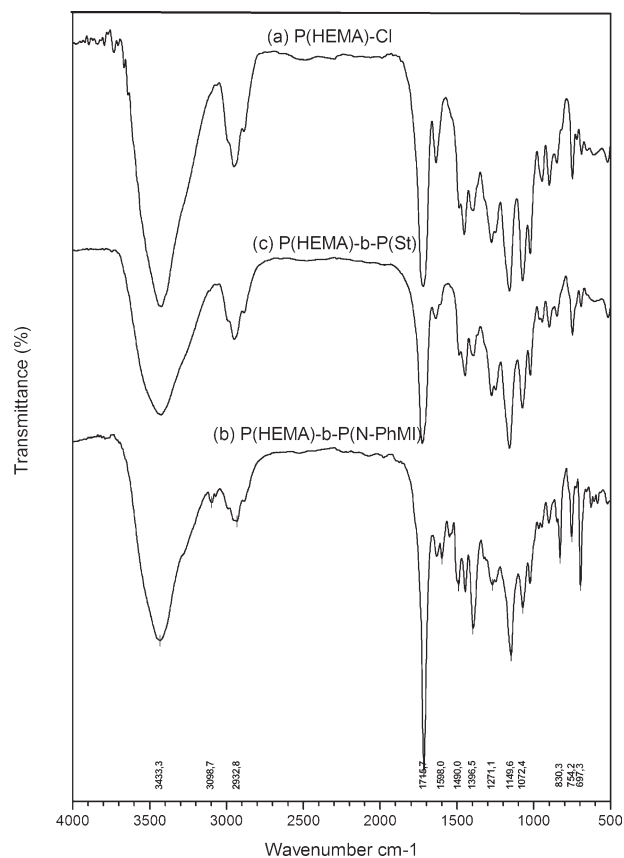


Figure 3 FTIR spectrum for P(HEMA)-Cl (a), P(HEMA)-*b*-P(N-PhMI)(b), and P(HEMA)-*b*-P(St)(c).

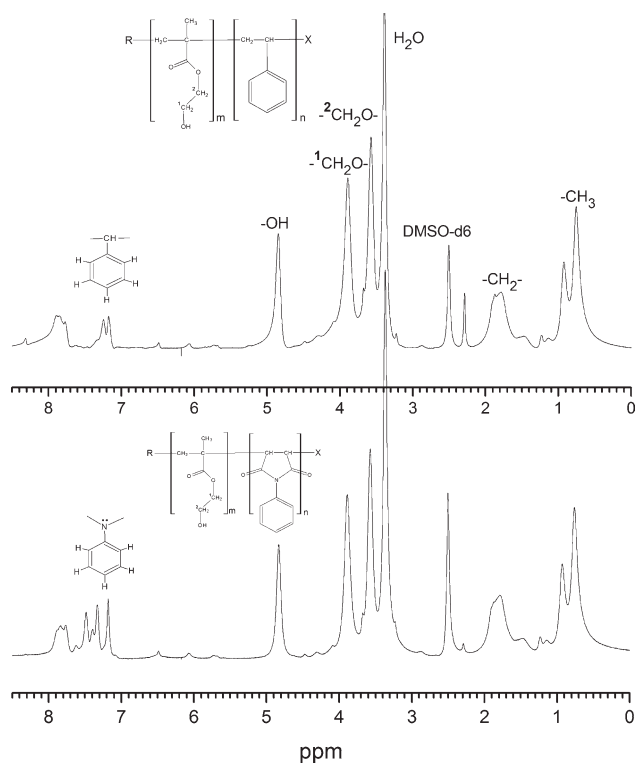


Figure 4 $^1\text{H-NMR}$ ($\text{DMSO-}d_6$) for block copolymers $\text{P(HEMA)-}b\text{-P(St)}$ and $\text{P(HEMA)-}b\text{-P(N-PhMI)}$ respectively.

reaction at 100°C ; high conversions were achieved after 8 h, but with low yield, indicating an uncontrolled process. Therefore, 90°C was found to be the most efficient temperature for the controlled radical copolymerization of HEMA, with a high conversion (80–90%) at 8 h of reaction.

The $^1\text{H-NMR}$ spectra ($\text{DMSO-}d_6$; δ ppm) for the block copolymers clearly showed the resonance signals at: 0.4–1.2 [3H, $-\text{CH}_3$]; 1.2–2.2 [2H, $-\text{CH}_2$ from the backbone and 1H, $-\text{CH}-$ from imide]; 2.5 and 3.3 solvent signals $\text{DMSO-}d_6$ and water, 3.4–4.2 [4H, $-\text{CH}_2$ side chain respectively from HEMA]; 4.8 [1H, $-\text{OH}$]; 7.7–7.6 [5H, $-\text{CH}$ aromatic protons from imide], 7.6–8.0 [aromatic protons from initiator] (Fig. 4). The $^{13}\text{C-NMR}$ ($\text{DMSO-}d_6$) spectra exhibits the following signals at (δ , ppm): 18 [$-\text{CH}_3$]; 40 solvent, 45 [$-\text{CH}_2$ from the principal backbone,]; 50–55 [$-\text{CH}$, $-\text{C}-$ backbone from imide and HEMA respectively]; 60–68 [$-\text{CH}_2$ side chain from HEMA]; 128–138 [$-\text{CH}$ aromatic ring], 170 and 178 [$-\text{C}=\text{O}$ from imide and HEMA, respectively] (Fig. 5).

The FTIR spectrum (KBr , cm^{-1}) for $\text{P(HEMA)}_{80}\text{-}b\text{-P(N-PhMI)}_{20}$, exhibits the most characteristic absorption bands: at 3433.3 cm^{-1} [$\nu(\text{OH})$]; at 2932.7 cm^{-1} [$\nu(\text{CH}, \text{CH}_2)$]; at 1719.6 cm^{-1} [$\nu(-\text{C}=\text{O})$]; 1633.7 cm^{-1} [$\nu(-\text{C}=\text{O}, \text{ester})$], 1396.4 cm^{-1} [$\nu(\text{N}-\text{C}, \text{imide ring})$], 754.1 and 697.2 cm^{-1} [$\nu(\text{aromatic ring})$] [Fig. 5(b)].

The copolymer composition was determined from elemental analysis data for the first system and $^1\text{H-NMR}$ for the entire system, Table III. The copolymers are soluble in acetone, DMF, and dimethylsulfoxide.

$\text{P(HEMA)-}b\text{-P(St)}$ using $\text{P(HEMA)-Cl/CuBr/bpy}$

The block copolymers were characterized using FTIR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ spectroscopy, and SEM. Thermal characterization was performed using differential scanning calorimetry (DSC) and thermogravimetry (TG). The temperature effect on ATRP was also investigated comparing the polymerization at 90 and 100°C for 8 h of reaction. The block copolymers synthesized at different temperatures exhibit a similar reaction and conversion behavior. The experimental polymerization conditions and results are shown in Table II. Copolymer composition was determined from E.A and $^1\text{H-NMR}$ data, Table III. The copolymers are soluble in dimethylsulfoxide and DMF. The $^1\text{H-NMR}$ spectra ($\text{DMSO-}d_6$; δ ppm) of the block copolymers clearly showed the resonance signals at: 0.6–1.4 [3H, $-\text{CH}_3$]; 1.6–2.2 [2H, $-\text{CH}_2$, and 1H, $-\text{CH}-$ of the backbone from HEMA and 2H, $-\text{CH}_2$ from styrene]; 2.7 and 3.4 ($\text{DMSO-}d_6$ and water), 3.7–3.9 [4H, $-\text{CH}_2$ side chain from HEMA]; 4.9 [1H, $-\text{OH}$]; 7.1–7.3 [5H, $-\text{CH}$ aromatic protons of styrene], 7.7–8.0 [aromatic protons from initiator] (Fig. 3). The $^{13}\text{C-NMR}$ spectra ($\text{DMSO-}d_6$; δ ppm) of the block copolymers clearly showed the resonance signals at: 16.6 [$-\text{CH}_3$]; 18.5 [$-\text{CH}_2$ from the backbone of styrene]; 40.3 solvent ($\text{DMSO-}d_6$), 44.5–55 [$-\text{CH}_2$ from the backbone of HEMA], 59.1 and 66.7 [$-\text{CH}_2$ side chain respectively from HEMA]; 128–135 [$-\text{CH}$ aromatic protons of styrene], 177 [$\text{C}=\text{O}$ from HEMA] (Fig. 4). The FTIR spectrum

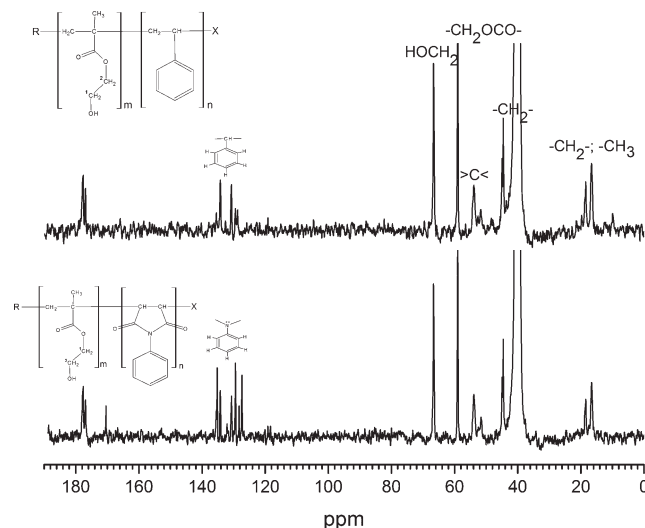


Figure 5 $^{13}\text{C-NMR}$ ($\text{DMSO-}d_6$) for block copolymers $\text{P(HEMA)-}b\text{-P(St)}$ and $\text{P(HEMA)-}b\text{-P(N-PhMI)}$ respectively.

(KBr, cm^{-1}) for P(HEMA)₉₀-*b*-P(St)₁₀, copolymer 7, exhibits the most characteristic absorption bands: at 3425.6 cm^{-1} [$\nu(\text{OH})$]; at 2951.1 cm^{-1} [$\nu(\text{CH}, \text{CH}_2)$]; at 1723.6 cm^{-1} [$\nu(-\text{C}=\text{O}, \text{ester})$], 749.3 and 693.4 cm^{-1} [$\nu(\text{stretching aromatic ring})$] [Fig. 5(c)].

Scanning electron microscopy (SEM)

The typical microphotographs by SEM of the P(HEMA)₉₀-*b*-P(St)₁₀ and P(HEMA)₈₀-*b*-P(N-PhMI)₂₀ are shown in Figures 6(a–c) respectively for a characteristic film. The SEM microphotographs in Figure 6(a,b) show that the film's upper surfaces were generally smooth, while the SEM for the bottom layer showed random distribution of chains that were continuously distributed within the matrix indicating a block copolymer. The upper surface layer of the P(HEMA)₈₀-*b*-P(N-PhMI)₂₀ films [see Fig. 6(c)] showed a less smooth structure in comparison with the upper surface layer of the block copolymer P(HEMA)₉₀-*b*-P(St)₁₀ films.

Thermal behavior

The TGA results for P(HEMA)-Cl and block copolymers P(HEMA)-*b*-P(N-PhMI) and P(HEMA)-*b*-P(St) are summarized in Table IV. The block copolymers and the macroinitiator systems exhibited different degradation steps. The TGA curves for P(HEMA)-Cl and block copolymers with different segment lengths are given in Figure 7. The resulting materials have an extrapolated thermal decomposition temperature (TDT) of about 300°C . The TDT of the block copolymers P(HEMA)₈₀-*b*-P(N-PhMI)₂₀ and P(HEMA)₉₀-*b*-P(St)₁₀ were about 290°C , which were also lower than for the macroinitiator. The P(HEMA)-Cl exhibited one-step degradation with TDT of 300°C , (curve 3), the polymer lost 10% of its weight from original weight (water, or some small molecular monomer trapped). The block copolymer systems, P(HEMA)₈₀-*b*-P(N-PhMI)₂₀ showed two-step degradation. The first step in the temperature range of $290\text{--}300$ is attributed to the introduction of the N-PhMI block (curve 4); the second step above 390°C can be due to HEMA block of the backbone chain. The P(HEMA)₈₀-*co*-P(St)₂₀ also exhibited two-steps degradation, with TDT₁ at 290°C is attributed to St segment's TDT and a less-pronounced TDT₂ at 350°C attributed to HEMA segment's TDT, (curve 7) respectively. The block copolymers synthesized at different temperatures exhibit a similar decomposition reaction.

The phase transition temperatures of the polymers were examined by DSC under N_2 . To eliminate the effect of thermal history on the phase transitions, all the samples were heated to 200°C , held at the temperature for 1 min and then rapidly cooled down to

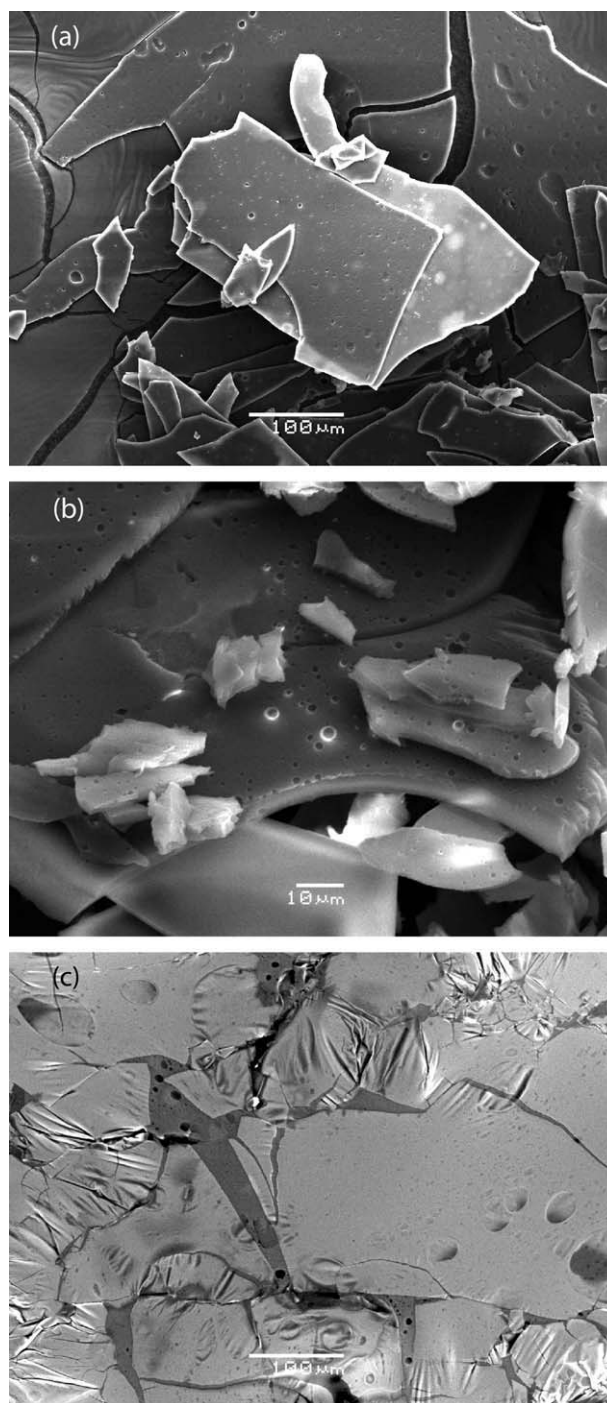


Figure 6 SEM micrograph (a,b) of P(HEMA)-*b*-P(St) show that the top surfaces of the film were generally smooth, (c) SEM microphotographs shows the film's surfaces of P(HEMA)-*b*-P(N-PhMI), which exhibit a internal structure less smooth.

-100°C with liquid nitrogen. The DSC results for P(HEMA)-Cl and diblock copolymers P(HEMA)₉₀-*b*-P(St)₁₀ and P(HEMA)₈₀-*b*-P(N-PhMI)₂₀ are summarized in Table V and given in Figures 8. The diblock copolymers and the macroinitiator systems exhibited different T_g temperatures. The DSC for poly

TABLE IV
Thermal Decomposition Temperature (TDT) and Weight Loss for P(HEMA)-Cl and Block Copolymers at Different Temperatures

Sample	Copolymer composition P(HEMA)/PM ₂	TDT ₁ TDT ₂ (°C)	Weight loss (%) at different temperatures (°C)				
			100	200	300	400	500
1)P(HEMA)-Cl	100	283.7	2.5	8.8	19.3	47.4	88.7
4)P(HEMA)- <i>b</i> -P(<i>N</i> -PhMI)	80 : 20	288.1 395.8	3.1	10.9	20.5	48.9	83.0
5)P(HEMA)- <i>b</i> -P(<i>N</i> -PhMI)	84 : 16	290.2 398.3	2.5	9.6	18.8	47.3	83.2
7)P(HEMA)- <i>b</i> -P(St)	90 : 10	290.8 390.0	3.0	10.7	22.1	67.0	90.7
8)P(HEMA)- <i>b</i> -P(St)	92 : 8	291.9 391.4	1.8	7.1	17.3	57.4	88.3

TDT, extrapolated thermal decomposition temperature.

(HEMA)-Cl exhibits a T_g of 91.2°C; the block copolymers P(HEMA)₈₀-*b*-P(*N*-PhMI)₂₀ exhibited a T_g of 101.3°C and the block copolymer P(HEMA)₉₀-*b*-P(St)₁₀ with different segment lengths exhibited a $T_g = 100.7$ °C. For the block copolymers, there is only one T_g before thermal decomposition, which could be attributed to the low molar content of the *N*-PhMI or St blocks respectively. On the other hand, the formation of the block copolymer affects the T_g of the HEMA block. The T_g of the P(HEMA)₈₀-*b*-P(*N*-PhMI)₂₀ increased and the T_g of the P(HEMA)₉₀-*b*-P(St)₁₀ decreased respect to HEMA block. This result also indicates that the phase behavior of the copolymers is predominately determined by the HEMA block. The curves reveal that the polymers show phase transition behavior of amorphous polymers.

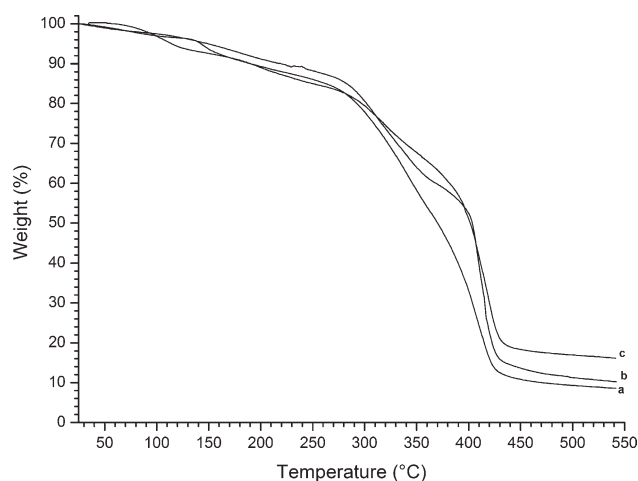


Figure 7 TGA thermograms of P(HEMA)-Cl (a), P(HEMA)-*b*-P(*N*-PhMI) (b), and P(HEMA)-*b*-P(St) (c). Heating rate: 10°C min⁻¹.

CONCLUSIONS

The controlled reverse ATRP of HEMA at 80°C, halogen-terminated, P(HEMA)-Cl was obtained in solution with BPO/FeCl₃·6H₂O/PPh₃ catalyst, resulting in the corresponding of amphiphilic block copolymers using ATRP. The theoretical number average molecular weight ($M_{n,th}$) was calculated from the feed capacity. The most interesting feature of the solvent polymerization system is that hydrophobic monomers can also be block-copolymerized in the same solvent allowing the direct synthesis of hydrophilic-hydrophobic block copolymers without protecting group chemistry, demonstrating the amphiphilic nature of these products.

The microphotographs of the film's surfaces show that the film's upper surfaces were generally smooth. The P(HEMA)₈₀-*b*-P(*N*-PhMI)₂₀ film's upper surface layer was less smooth in comparison with the upper surface layer of the block copolymer P(HEMA)₉₀-*b*-P(St)₁₀.

The resulting materials have an extrapolated thermal decomposition temperature (TDT) of about 300°C. The TDT of the block copolymer P(HEMA)₈₀-*b*-P(*N*-PhMI)₂₀ and P(HEMA)₉₀-*b*-P(St)₁₀ of about 290°C were also lower than found for the macroinitiator poly(HEMA)-Cl.

TABLE V
Glass Transition Temperature (T_g) and Heat Capacity (ΔC_p) of macroinitiator and Block copolymers

Sample no	Polymer	ΔC_p (J/g K)	T_{g1} (°C)	T_{g2} (°C)
3	P(HEMA)-Cl	0.355	—	91.2
4	P(HEMA) ₈₀ - <i>b</i> -P(<i>N</i> -PhMI) ₂₀	0.207	0.327	101.3
7	P(HEMA) ₉₀ - <i>b</i> -P(St) ₁₀	0.261	—	84.7

T_{g1} , Glass transition temperature; ΔC_p , heat capacity of the T_g .

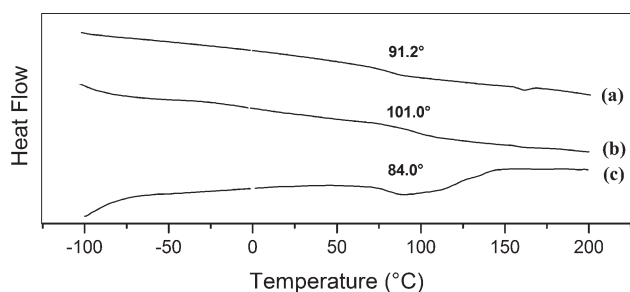


Figure 8 DSC thermograms show the T_g of the P(HEMA)-Cl (a); P(HEMA)-*b*-P(*N*-PhMI) (b); P(HEMA)-*b*-P(St) (c). Heating rate: $10^\circ\text{C min}^{-1}$.

The DSCs for the poly(HEMA)-Cl exhibit a T_g of 91.2°C . For the block copolymers, there is only one T_g before thermal decomposition, which could be attributed to the low molar content of the *N*-PhMI or St blocks respectively. On the other hand, the formation of the block copolymer affects the T_g of the HEMA block. This result also indicates that the phase behavior of the copolymers is predominately determined by the HEMA block. The curves reveal that the polymers show phase transition behavior of amorphous polymers.

References

- Anand, V.; Agarwal, S.; Greiner, A.; Choudhary, V. *Polym Int* 2005, 54, 823.
- Webster, O. W. *Makromol Chem Macromol Symp* 1990, 33, 133.
- Lohmeijer, B. G. G.; Schubert, U. S. *J Polym Sci Part A: Polym Chem* 2004, 42, 4016.
- Gopalan, P.; Li, X.; Li, M.; Ober, C. K.; Gonzales, C. P.; Hawker, C. J. *J Polym Sci Part A: Polym Chem* 2003, 41, 3640.
- Matsuno, R.; Yamamoto, K.; Otsuka, H.; Takahara, A. *Macromolecules* 2004, 37, 2203.
- Huang, J. Y.; Pintauer, T.; Matyjaszewski, K. *J Polym Sci Part A: Polym Chem* 2004, 42, 3285.
- Lutz, J. F.; Jahed, N.; Matyjaszewski, K. *J Polym Sci Part A: Polym Chem* 2004, 42, 1939.
- Sarbu, T.; Lin, K. Y.; Ell, J.; Siegwart, D. J.; Spanswick, J.; Matyjaszewski, K. *Macromolecules* 2004, 37, 3120.
- Hao, X. J.; Nilsson, C.; Jesberger, M.; Stenzel, M. H.; Malmström, E.; Davis, T. P.; Östmark, E.; Barner-Kowollik, C. *J Polym Sci Part A: Polym Chem* 2004, 42, 5877.
- Hong, C. Y.; You, Y. Z.; Pan, C. Y. *J Polym Sci Part A: Polym Chem* 2004, 42, 4873.
- Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* 1998, 31, 5559.
- Schilli, C. M.; Zhang, M. F.; Rizzardo, E.; Thang, S. H.; Chong, Y. K.; Edwards, K.; Karlsson, G.; Muller, A. H. E. *Macromolecules* 2004, 37, 7861.
- Beers, K. L.; Boo, S.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* 1999, 32, 5772.
- Weaver, J. V. M.; Bannister, I.; Robinson, K. L.; Bories-Azeau, X.; Armes, S. P.; Smallridge, M.; McKenna, P. *Macromolecules* 2004, 37, 2395.
- Yin, M.; Habicher, W. D.; Voit, B. *Polymer* 2005, 46, 3215.
- Cava, M. P.; Deana, A. A.; Muth, K.; Mitchell, M. J. *Synthesis* 1961, 41, 93.