

# Atom Transfer Radical Polymerization of Styrene and Methyl (Meth)acrylates Initiated with Poly(dimethylsiloxane) Macroinitiator: Synthesis and Characterization of Triblock Copolymers

Mohammad Ali Semsarzadeh, Mahdi Abdollahi

*Polymer Engineering Department, Faculty of Chemical Engineering, Tarbiat Modares University, Tehran, Iran*

Received 20 February 2011; accepted 27 April 2011

DOI 10.1002/app.34794

Published online 24 August 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Poly(dimethylsiloxane)(PDMS)-based triblock copolymers were successfully synthesized via atom transfer radical polymerization (ATRP) initiated with bis(bromoalkyl)-terminated PDMS macroinitiator (Br-PDMS-Br). First, Br-PDMS-Br was prepared by reaction between the bis(hydroxyalkyl)-terminated PDMS and 2-bromo-2-methylpropionyl bromide. PSt-*b*-PDMS-*b*-PSt, PMMA-*b*-PDMS-*b*-PMMA and PMA-*b*-PDMS-*b*-PMA triblock copolymers were then synthesized via ATRP of styrene (St), methyl methacrylate (MMA) and methyl acrylate (MA), respectively, in the presence of Br-PDMS-Br as a macroinitiator and CuCl/PMDETA as a catalyst system at 80 °C. Triblock copolymers were characterized by FTIR, <sup>1</sup>H-NMR and GPC techniques. GPC results showed linear dependence of the number-average molecular weight on

the conversion as well as the narrow polydispersity indices (PDI < 1.57) for the synthesized triblock copolymers which was lower than that of Br-PDMS-Br macroinitiator (PDI = 1.90), indicating the living/controlled characteristic of the reaction. Also, there was a very good agreement between the number-average molecular weight calculated from <sup>1</sup>H-NMR spectra and that calculated theoretically. Results showed that resulting copolymers have two glass transition temperatures, indicating that triblock copolymers have microphase separated morphology. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2423–2430, 2012

**Key words:** atom transfer radical polymerization (ATRP); styrene; methyl (meth)acrylate; PDMS macroinitiator; triblock copolymer

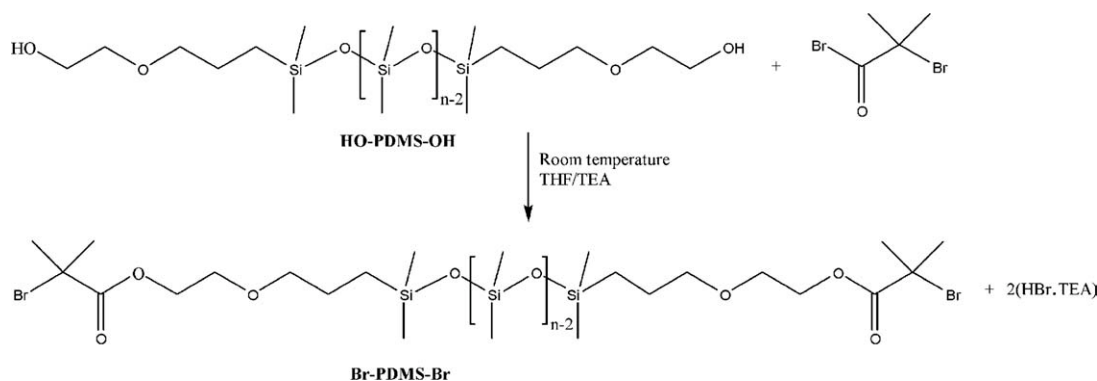
## INTRODUCTION

Development of the controlled/ living radical polymerization (CLRP) for synthesis of the polymers with controlled architecture, molecular weight, and narrow polydispersity is among the most significant accomplishments in the polymer chemistry.<sup>1–3</sup> Among three kinds of CLRP methods, atom transfer radical polymerization (ATRP) is one of the most successful methods to polymerize styrenes, methacrylates, acrylates and a variety of other monomers in a controlled fashion.<sup>1–3</sup> The development of ATRP has opened a way to a real macromolecular engineering of polymeric materials<sup>4</sup> and a new route for the controlled synthesis of several block copolymers.<sup>5,6</sup> A wide variety of the block copolymers can be derived from the same family of vinyl monomers or different families of vinyl monomers via ATRP.<sup>7,8</sup>

Silicone-based copolymers have successfully been synthesized by ATRP. In most of the cases, silicones are used as coatings or additives because of their unique surface properties. For instance, silicones are used as paper release or metal protector in the case of coating applications, or as additives in the fields of antifoams and paints.<sup>9</sup> Polydimethylsiloxane (PDMS) is undoubtedly the most widely used silicone, which is characterized by a unique combination of properties such as low surface tension, low glass transition temperature, high permeability to gas, and excellent weather resistance. Its wide range of applications such as polyurethane foam stabilization, release coatings, and pressure-sensitive adhesives illustrates the versatility of this organo-element polymer. However, since PDMS is a fluid at room temperature, the homopolymer lacks dimensional stability. To produce silicone-based materials with more desirable mechanical properties, block, graft, and network copolymers containing PDMS segments have been investigated.<sup>10–13</sup> Copolymers containing PDMS are usually hydrophobic and exhibit properties such as gas permeability, low irritation potential, low melting and glass-transition temperatures, very low surface tension,<sup>14,15</sup> and, probably most important, nontoxic and environmentally compatible. These copolymers can be used as surfactants,

Correspondence to: M. A. Semsarzadeh (semsarzadeh@modares.ac.ir).

Contract grant sponsors: Scientific Center of Excellence in Chemical Engineering by Ministry of Science and Technology, Faculty of Chemical Engineering, Tarbiat Modares University, Tehran, Iran.



**Scheme 1** Reaction scheme for synthesis of bis(2-bromoisobutyrate)-terminated PDMS macroinitiator from bis(hydroxyalkyl)-terminated PDMS.

lubricants, water repellents, and antifoaming agents.<sup>16–18</sup> For example, advantage of the solubility of PDMS in supercritical carbon dioxide (scCO<sub>2</sub>) has been taken to use PDMS-*b*-polystyrene (PDMS-*b*-PSt) diblock copolymer as a steric stabilizer for dispersion polymerization in scCO<sub>2</sub>.<sup>19,20</sup> Such block and graft copolymers can be prepared using free radical polymerization. For example, PDMS containing internal tetraphenylethylene moieties was used for the synthesis of segmented multiblock copolymers with various vinyl monomers.<sup>21,22</sup> Although the use of macroinitiators for free radical polymerization appeared to be very promising, conventional methods introduced problems such as limited end-group functionalization, incomplete initiation efficiency and homopolymer formation.<sup>23,24</sup>

These problems are avoided by performing iodine transfer polymerization (ITP) or ATRP from PDMS macroinitiators. Diblock and triblock copolymers containing PDMS segment have been synthesized by ATRP of styrene and (meth)acrylates initiated with mono- or bi-functional PDMS macroinitiators, respectively.<sup>25–35</sup> Hydride, chloride, aminopropyl and vinyl-terminated PDMSs have been used as starting materials to prepare alkyl halide-terminated PDMS as a suitable ATRP macroinitiator.<sup>25–32</sup> PDMS macroinitiator has then been used in the ATRP of monomers such as St, methyl methacrylate (MMA), *n*-butyl methacrylate (BMA) and *n*-butyl acrylate (BA) to prepare AB and BAB block copolymers (PDMS is designated as the A segment) of PDMS-*b*-PSt,<sup>25–27</sup> PDMS-*b*-PBA,<sup>27</sup> PMMA-*b*-PDMS-*b*-PMMA,<sup>27–29</sup> PSt-*b*-PDMS-*b*-PSt,<sup>26,28,30,31</sup> PBMA-*b*-PDMS-*b*-PBMA.<sup>32</sup> Recently, monocarbinol (i.e. mono-hydroxyalkyl)-terminated PDMS has been functionalized by 2-bromo-2-methylpropionyl bromide. Then, resulting alkyl bromide-terminated PDMS macroinitiator has been used in the ATRP of ethyl methacrylate (EMA),<sup>33</sup> MMA, BMA, 2-ethylhexyl methacrylate<sup>34</sup> and 2,2,3,3,4,4,4-heptafluorobutyl methacrylate<sup>35</sup> to prepare corresponding PDMS-based diblock copolymers.

Bis(alkyl iodide)-terminated PDMS has been synthesized from Bis(hydroxyalkyl)-terminated PDMS and then used as a macroinitiator in the ITP of St and vinyl acetate (VAc) to prepare triblock copolymers of PSt-*b*-PDMS-PSt and PVAc-*b*-PDMS-*b*-PVAc.<sup>36,37</sup> To our knowledge, there is no report on using bis(hydroxyalkyl)-terminated PDMS as a starting material to prepare bifunctional ATRP macroinitiator. It is expected that bis(hydroxyalkyl)-terminated PDMS can readily be converted to the bis(alkyl halide)-terminated PDMS. Also, PDMS-based block copolymer containing poly (methyl acrylate) (PMA) segment has not been reported in the literature. It is expected that PMA-*b*-PDMS-PMA triblock copolymer can be used as a membrane for gas separation. The aim of this work is to prepare bis(2-bromoisobutyrate)-terminated PDMS macroinitiator from bis(hydroxyalkyl)-terminated PDMS for the first time and then use it as a macroinitiator in the ATRP of St, MMA, and MA for preparing the corresponding PDMS-based triblock copolymers. The synthesized triblock copolymers are characterized by FTIR, <sup>1</sup>HNMR, DSC, and gel permeation chromatography (GPC).

## EXPERIMENTAL SECTION

### Materials

Bis(hydroxyalkyl)-terminated PDMS (HO-PDMS-OH) with average molecular weight of 5600 g mol<sup>-1</sup> (a value reported by manufacturer) was obtained from Aldrich and used without further purification. According to its molecular weight and data reported in the literature,<sup>38,39</sup> microstructure of HO-PDMS-OH can be shown as HO-R-PDMS<sub>70</sub>-R-OH (see Scheme 1 with *n* ~ 70). 2-bromo-2-methylpropionyl bromide (Aldrich, 98%), triethylamine (TEA) (Sigma-Aldrich, = 99.5%), anhydrous tetrahydrofuran (THF) (Sigma-Aldrich, = 99.9%, inhibitor-free), dichloromethane (Sigma-Aldrich, = 98%), anhydrous toluene (Sigma-Aldrich, 99.8%), anhydrous magnesium

sulfate (Sigma-Aldrich, = 99.5) and sodium bicarbonate (Fluka, = 99%) were used as received. St (Merck, > 99%), MMA (Merck, > 99%) and MA (Merck, 99%) were distilled over calcium hydride under reduced pressure before use. CuCl (Merck, 97%) was washed by glacial acetic acid (three times), absolute ethanol and diethyl ether in turn and then dried under vacuum. *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) (Merck, 99.8%) was used as received.

### Preparation of PDMS macroinitiator (Br-PDM-Br)

First, a solution of HO-PDMS-OH (24.64 g, 4.4 mmol) in the anhydrous THF (800 ml) was prepared and placed in the three-neck round-bottomed flask. Triethylamine (6.18 ml, 44.4 mmol) was added to the solution followed by slowly adding of 2-bromo-2-methylpropionyl bromide (2.74 ml, 22.2 mmol) at 0°C with stirring. The solution was left overnight at room temperature (Scheme 1). The triethylammonium bromide salt was removed by filtration of solution and the solvent was then removed under vacuum. The resulting oil (yellow in color) was redissolved in dichloromethane (800 mL) and washed two times with saturated sodium bicarbonate solution (400 mL). The organic layer was isolated, dried over anhydrous magnesium sulfate and filtered. Then, the final product was obtained as oil after removing volatiles under vacuum (yield = 87 wt %).<sup>29,33</sup>

### ATRP of St, MMA, and MA with Br-PDMS-Br macroinitiator

The PDMS-based triblock copolymers were synthesized by copper (I)-mediated ATRP of St, MMA, and MA initiated by the Br-PDMS-Br macroinitiator according to the following typical procedure.

A required amount of CuCl (0.70 mmol, 0.069 g) was introduced into the three-neck round-bottomed flask equipped with a magnetic stirrer. The flask was sealed with a rubber septum and was cycled between vacuum and nitrogen three times. Mixtures containing required amounts of monomer (70 mmol, i.e. 7.290 g, 7.008 g, or 6.026 g from St, MMA or MA respectively), Br-PDMS-Br macroinitiator (0.35 mmol, 2.012 g) and PMDETA ligand (1.40 mmol, 0.243 g) were degassed by purging nitrogen for 30 min and then added to the flask. The molar ratio of reaction ingredients  $[\text{Monomer}]_0/[\text{PMDETA}]_0/[\text{CuCl}]_0/[\text{Br-PDMS-Br}]_0$  was kept constant for all experiments (200/4/2/1). It should be noted that in the case of MMA polymerization, degassed toluene (10 mL) was also added as a solvent to the reaction mixture. The "freeze-pump-thaw" cycle was carried out three times to remove oxygen from the flask

containing reaction mixture. Flask was sealed under vacuum and then immersed in a preheated oil bath at a desired temperature (i.e.,  $80 \pm 0.1^\circ\text{C}$ ). Depending on the monomer used, reaction mixture was removed at the given reaction time from the oil bath and diluted with THF, filtered, and dried under vacuum to a constant weight. The dried copolymer was redissolved in THF and passed through a short column of neutral alumina to remove the remaining copper catalyst. The samples were then dried under vacuum at  $50^\circ\text{C}$  up to a constant weight and used in FTIR,  $^1\text{H}$ NMR, DSC, and GPC analyses. Conversion of the monomers St, MMA, and MA was determined gravimetrically to be 53.1, 85.0, and 32.9%, respectively.

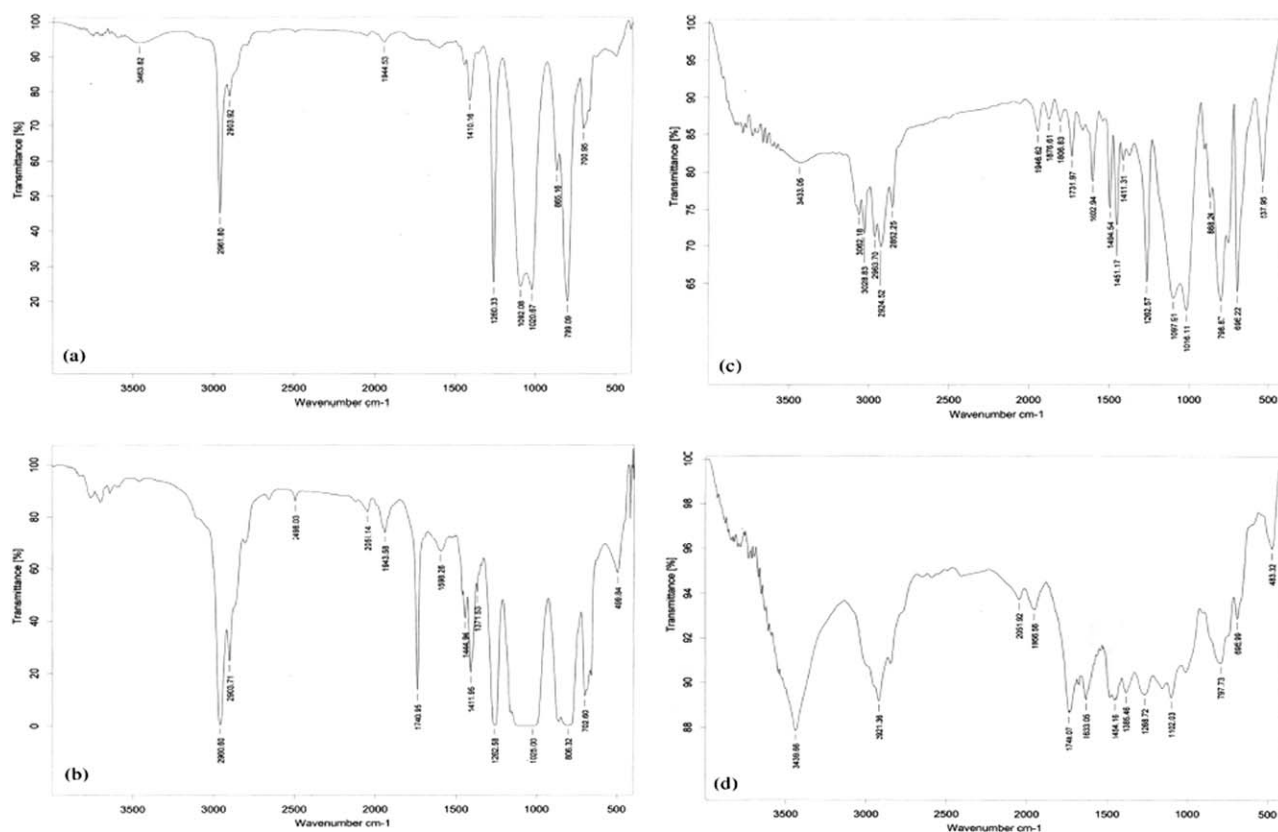
### Characterization

Mass conversion of monomers (*X*) was calculated gravimetrically. PDMS-based triblock copolymers were dissolved in  $\text{CDCl}_3$  and characterized by 400 MHz  $^1\text{H}$ NMR spectroscopy (DRX 400 Bruker Avance) at ambient temperature. Polymer concentration in the  $\text{CDCl}_3$  solution was about 2 w/v %. Fourier transform infrared (FTIR) spectrum of the HO-PDMS-OH (liquid), Br-PDMS-Br (liquid) and triblocks (solids) was recorded on an EQUINOX 55 Bruker FTIR Spectrophotometer. Apparent (i.e., polystyrene-equivalent) molecular weight and polydispersity of the terpolymers dissolved in THF was determined by a Waters 150C gel permeation chromatography (GPC) equipped with a  $10^4$ ,  $10^3$ , and 500 Å set of Ultrastaygel columns and a refractive index (RI) detector. Polystyrene standards with the narrow molecular weight distributions and molecular weights in the range of analyzed molecular weights were used to calibrate the columns. THF was used as an eluent with the flow rate of 1 mL/min at  $35^\circ\text{C}$ . Differential scanning calorimetry (DSC) measurements were performed by a Netzsch DSC 200 apparatus at two temperature variation rates of  $20^\circ\text{C}/\text{min}$  for the heating and cooling runs and  $10^\circ\text{C}/\text{min}$  for the final reheating run.

## RESULTS AND DISCUSSION

### Synthesis of the Br-PDMS-Br macroinitiator

PDMS-based triblock copolymers can be prepared from commercially available PDMS materials with appropriate functionality at one or two ends. It is then possible to transform the end group(s) into active polymerization (macro)initiators. For example, hydride, chloride, aminopropyl, monocarbinol (i.e., monohydroxyalkyl) and vinyl-terminated PDMSs have been used as starting materials to prepare alkyl halide-terminated PDMS as a suitable ATRP



**Figure 1** FTIR spectra of HO-PDMS-OH (a), Br-PDMS-Br macroinitiator (b), PSt-*b*-PDMS-*b*-PSt (c), and PMMA-*b*-PDMS-*b*-PMMA (d) triblocks.

macroinitiator.<sup>25–35</sup> To our knowledge, there is no report on using bis(hydroxyalkyl)-terminated PDMS as a starting material to prepare bifunctional ATRP macroinitiator. In the present work, we used bis(hydroxyalkyl)-terminated PDMS as the starting material to synthesize bromoalkyl-terminated PDMS (Br-PDMS-Br) as macroinitiator for the ATRP of St, MMA or MA. The reaction was proceeded in a high yield (88 wt %).

FTIR and <sup>1</sup>H-NMR spectra of HO-PDMS-OH and Br-PDMS-Br macroinitiator have been shown in Figures 1 and 2, respectively. FTIR spectra of both compounds show presence of the “C-Si-C” absorption band at about 800 cm<sup>-1</sup>, the “Si-O-Si” absorption band at about 1020 cm<sup>-1</sup> and the “CH<sub>3</sub>” absorption band at about 1260 cm<sup>-1</sup> as characteristics of the PDMS segment. Additional absorption band appeared at about 1740 cm<sup>-1</sup> [Fig. 1(b)] was assigned to the carbonyl (C=O) absorption bond, indicating that the bromoalkyl-terminated PDMS has successfully been synthesized by the reaction between bis(hydroxyalkyl)-terminated PDMS and 2-bromo-2-methylpropionyl bromide. All <sup>1</sup>H-NMR signals were assigned to the corresponding protons (Fig. 2). Quantitative shift of the signal at about 3.7 ppm (assigned to the -CH<sub>2</sub>-OH methylene protons) in favor of a new signal appeared at about 4.3 ppm (assigned to the -CH<sub>2</sub>-O-CO- methylene protons) and appearance of

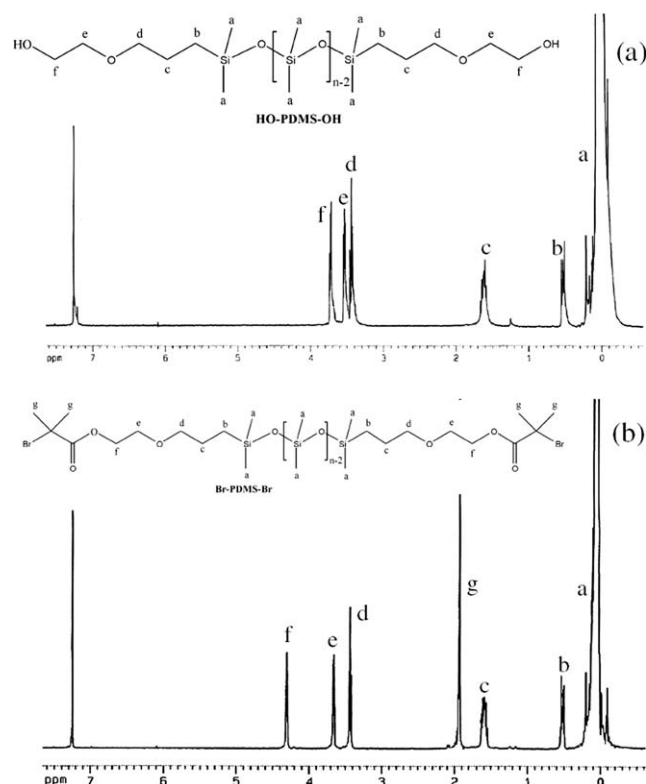
sharp signal at about 1.9 ppm (assigned to the -C(Br)(CH<sub>3</sub>)<sub>2</sub> methyl protons) was observed in the <sup>1</sup>H-NMR spectrum of Br-PDMS-Br macroinitiator [Fig. 1(b)] in comparison to that of HO-PDMS-OH [Fig. 1(a)], further confirming the quantitative reaction of the hydroxyl end groups of HO-PDMS-OH with 2-bromo-2-methylpropionyl bromide.

Number-average molecular weight of both HO-PDMS-OH and Br-PDMS-Br can be calculated from corresponding <sup>1</sup>H-NMR spectra [Fig. 2(a,b), respectively] via the following equations:

$$M_{n, \text{HO-PDMS-OH}} = \left( \frac{[I_a/6]}{[I_b/4]} \times 74.10 \right) + (2 \times 103.05) \quad (1)$$

$$M_{n, \text{Br-PDMS-Br}} = \left( \frac{[I_a/6]}{[I_b/4]} \times 74.10 \right) + (2 \times 251.99) \quad (2)$$

where  $I_a$  and  $I_b$  indicate signal intensities of -Si(CH<sub>3</sub>)<sub>2</sub>- methyl (present in the PDMS backbone) and -CH<sub>2</sub>-Si- methylene (present in the hydroxyalkyl end group) protons respectively. Values of 74.10, 103.05, and 252.99 indicate molecular weight of -Si(CH<sub>3</sub>)<sub>2</sub>-O- repeating unit, hydroxyalkyl end group in the HO-PDMS-OH and bromoalkyl end group in the Br-PDMS-Br (Scheme 1). It should be noted that  $[I_a/6]/[I_b/4]$  in the above equations indicates indeed



**Figure 2**  $^1\text{H}$ NMR spectra of HO-PDMS-OH (top) and Br-PDMS-Br macroinitiator (bottom) in the  $\text{CDCl}_3$  solvent.

number of the  $-\text{Si}(\text{CH}_3)_2-\text{O}-$  repeating units. Calculation results have been given in Table I.

Molecular weight and its distribution (i.e., polydispersity index, PDI) of the HO-PDMS-OH and Br-PDMS-Br macroinitiator were analyzed by GPC (Table I). There is a good agreement between the molecular weight obtained by GPC and  $^1\text{H}$ NMR analyses which in turn are also in good agreement with the molecular weight reported by manufacturer (Table I).

### Synthesis of the PDMS-based triblock copolymers

As already mentioned, bromoalkyl-terminated PDMS seems to be as a highly efficient ATRP macroinitiator for synthesizing the PDMS-based block copolymers via ATRP of various monomers such as styrenes and (meth)acrylates. Reaction scheme for the various PDMS-based triblock copolymers synthesized in the present study via the ATRP reaction in the presence of Br-PDMS-Br macroinitiator has been shown in Scheme 2. Chemical structure analysis (see the following section) revealed that well-defined PSt-*b*-PDMS-*b*-PSt, PMMA-*b*-PDMS-*b*-PMMA, and PMA-*b*-PDMS-*b*-PMA triblock copolymers are synthesized by the ATRP of St, MMA, or MA initiated with Br-PDMS-Br macroinitiator in the presence of  $\text{CuCl}/\text{PMDETA}$  catalyst system at  $80^\circ\text{C}$ .

Chemical structure of the triblock copolymers was analyzed by FTIR (Fig. 1) and  $^1\text{H}$ NMR (Fig. 3). It should be noted that FTIR spectrum of the PMA-*b*-PDMS-*b*-PMA has been omitted in the text due to its similarity with that of the PMMA-*b*-PDMS-*b*-PMMA. Figure 1(c,d) reveals that the block copolymers consist of PDMS segment located at the center and PSt and PMMA, respectively, segments located at the end sides of the triblock copolymers. The characteristic PDMS absorption bands of “Si-O-Si” at about  $1020\text{ cm}^{-1}$ , “ $\text{CH}_3$ ” at about  $1260\text{ cm}^{-1}$  and “C-Si-C” at about  $800\text{ cm}^{-1}$  are still present in the Figure 1(c,d). Moreover, the characteristic PSt absorption bands appeared at 696, 758, 2924, 3028, and  $3062\text{ cm}^{-1}$  [Fig. 1(c)] and the characteristic PMMA absorption bands appeared at 1740 and  $1178\text{ cm}^{-1}$  (ester group characteristic), indicating the successfully synthesis of PDMS-based triblock copolymers.

$^1\text{H}$ NMR spectra of the Br-PDMS-Br macroinitiator and the final triblock copolymers have been shown in Figures 2 and 3, respectively. All signals appeared in

**TABLE I**  
Summary of the Results Obtained from GPC and  $^1\text{H}$ NMR Analyses for HO-PDMS-OH, Br-PDMS-Br Macroinitiator, PSt-*b*-PDMS-*b*-PSt, PMMA-*b*-PDMS-*b*-PMMA, and PMA-*b*-PDMS-*b*-PMA Triblock

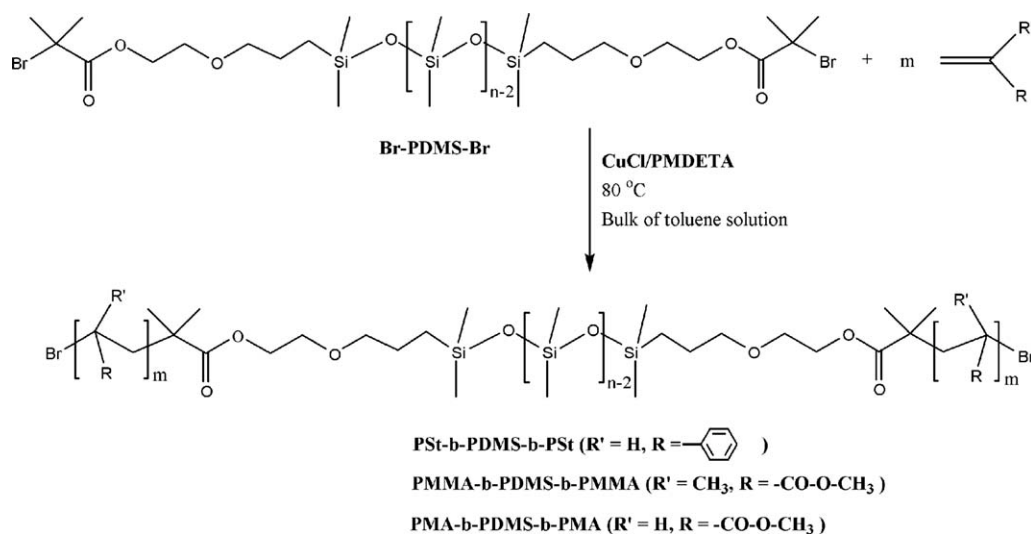
Sample	X (%) <sup>a</sup>	$\bar{M}_{n,\text{theor}}$ ( $\text{g mol}^{-1}$ )	$\bar{M}_{n,\text{NMR}}$ ( $\text{g mol}^{-1}$ )	$\bar{M}_{n,\text{GPC}}$ <sup>b</sup> ( $\text{g mol}^{-1}$ )	PDI
HO-PDMS-OH	–	5,600 <sup>c</sup>	5,258	5,135	1.79
Br-PDMS-Br	–	5,898 <sup>d</sup>	5,469	5,216	1.90
PSt- <i>b</i> -PDMS- <i>b</i> -PSt	53.1	16,530	16,396	19,511	1.57
PMMA- <i>b</i> -PDMS- <i>b</i> -PMMA	85.0	22,489	22,104	30,319	1.44
PMA- <i>b</i> -PDMS- <i>b</i> -PMA	32.9	11,134	11,358	16,538	1.48

<sup>a</sup> Final conversion measured by gravimetric method.

<sup>b</sup>  $\bar{M}_{n,\text{theor}} = \sum \left[ \left( \frac{[M]_0}{[\text{Br-PDMS-Br}]_0} \right) \times X \times M_{n,M} \right] + \bar{M}_{n,\text{Br-PDMS-Br}}$  in which  $[M]_0$ , X, and  $M_{n,M}$  are the molar concentration, conversion and molecular weight of monomer (St, MMA or MA) respectively and  $\bar{M}_{n,\text{Br-PDMS-Br}} = 5469\text{ g mol}^{-1}$ .

<sup>c</sup>  $\bar{M}_n$  value reported by manufacturer.

<sup>d</sup> This value was calculated via  $\bar{M}_{n,\text{Br-PDMS-Br}} = \bar{M}_{n,\text{HO-PDMS-OH}} + (2 \times 148.94)$  [see also eqs. (1) and (2)].



**Scheme 2** Reaction scheme for synthesis of the PDMS-based triblock copolymers

the  $^1\text{H}$ NMR spectra were assigned to the corresponding monomers. It is clear from Figure 3 that triblock copolymers have successfully been synthesized. The characteristic PDMS signal of  $\text{CH}_3\text{-Si}$  methyl protons at about 0.0–0.2 ppm was still present in all the spectra [Figs. 3(a–c)]. Additional broad signals at about 6.6–7.1 ppm and 1.2–2.3 ppm were observed in Figure 3(a), which were assigned to the phenyl ring protons and aliphatic protons, respectively, of the PSt segment. Additional signals were also observed in the  $^1\text{H}$ NMR spectra of two other triblock copolymers [see Figs. 3(b,c) and compare them with  $^1\text{H}$ NMR spectrum of Br-PDMS-Br in Fig. 2], which were assigned to the corresponding protons of monomers (MMA and MA, respectively) incorporated into the triblock copolymer chain. Therefore, it is possible to synthesize the PDMS-based triblock copolymers via ATRP of monomers such as styrenes and (meth)acrylates in the presence of bis(haloalkyl)-terminated PDMS macroinitiator.

Number-average molecular weight of the triblock copolymers can be calculated from corresponding  $^1\text{H}$ NMR spectra [Fig. 3(a–c)] via the following equations:

$$M_{n,\text{PSt-}b\text{-PDMS-}b\text{-PSt}} = \left( \frac{[I_{e+d}/5]}{[I_a/6]} \times 67 \times 104.15 \right) + M_{n,\text{Br-PDMS-Br}} \quad (3)$$

$$M_{n,\text{PMMA-}b\text{-PDMS-}b\text{-PMMA}} = \left( \frac{[I_d/3]}{[I_a/6]} \times 67 \times 100.12 \right) + M_{n,\text{Br-PDMS-Br}} \quad (4)$$

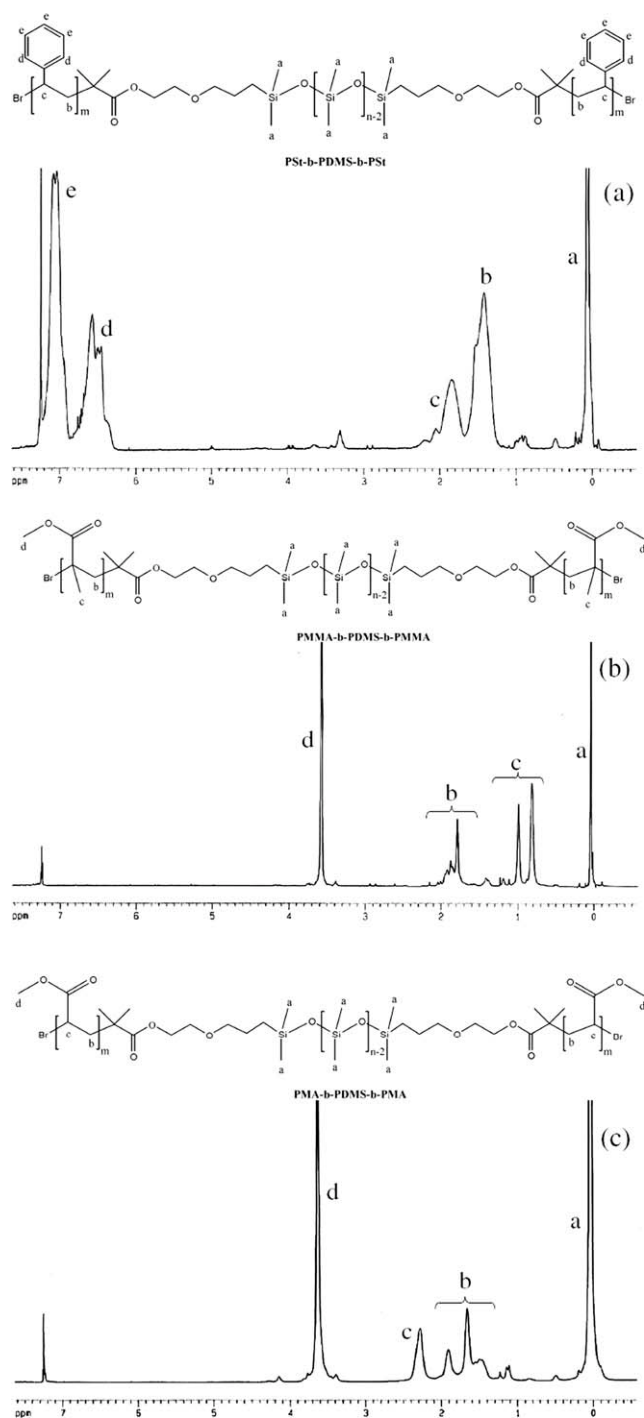
$$M_{n,\text{PMA-}b\text{-PDMS-}b\text{-PMA}} = \left( \frac{[I_d/3]}{[I_a/6]} \times 67 \times 86.09 \right) + M_{n,\text{Br-PDMS-Br}} \quad (5)$$

in which  $I_a$ ,  $I_{e+d}$ , and  $I_d$  indicate signal intensities of  $-\text{Si}(\text{CH}_3)_2$  methyl (from PDMS), phenyl ring (from

PSt) and  $-\text{OCH}_3$  methoxy (from PMMA or PMA) protons, respectively. Value of 67 indicates number of the  $-\text{Si}(\text{CH}_3)_2-\text{O}-$  repeating units in the Br-PDMS-Br macroinitiator, which has been calculated from the corresponding  $^1\text{H}$ NMR spectrum (Fig. 2) via eq. (2). Values of 104.15, 100.12 and 86.09 indicate molecular weight of monomers St, MMA, and MA respectively. Number-average molecular weight of Br-PDMS-Br obtained from  $^1\text{H}$ NMR ( $5469 \text{ g mol}^{-1}$ , Table I) was used in the eqs. (3)–(5). Summary of calculation results has been given in Table I. There is a very good agreement between the number-average molecular weight calculated from  $^1\text{H}$ NMR spectra and that calculated theoretically, indicating the living/controlled characteristic of the reaction.

Molecular weight and its distribution (i.e., PDI) of the triblock copolymers were measured by GPC (Table I and Fig. 4). It is clear from Table I and Figure 4 that number average molecular weights of the triblock copolymers measured by GPC analysis are higher than that measured by  $^1\text{H}$ NMR. However, this difference is not significant in the case of PSt-*b*-PDMS-*b*-PSt triblock copolymer. This can be explained by considering this fact that the GPC method provides only polystyrene-equivalent molecular weights due to its inability to distinguish the different nature of the incorporated monomers.

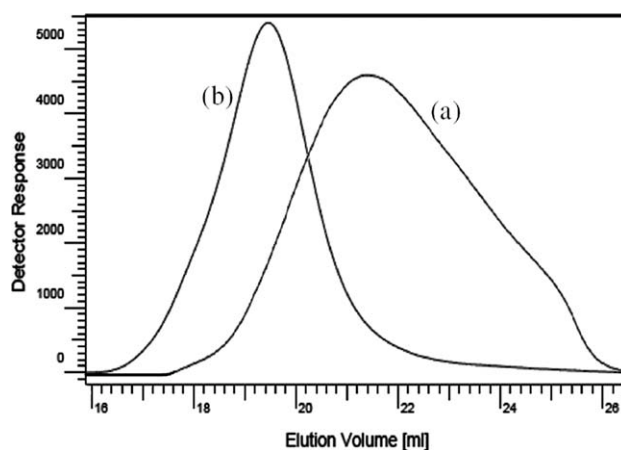
GPC results showed the narrow polydispersity indices ( $\text{PDI} < 1.57$ ) for the synthesized triblock copolymers at the final conversion which is lower than that of initial macroinitiator ( $\text{PDI} = 1.90$ ) (Table I), indicating the living/controlled characteristic of the reaction. Although experimental number-average molecular weight ( $M_{n,\text{GPC}}$ ) is relatively greater than theoretical one (Table I); however, dependence of  $M_{n,\text{GPC}}$  on the monomer conversion is linear and



**Figure 3**  $^1\text{H}$ NMR spectra of PSt-*b*-PDMS-*b*-PSt (a), PMMA-*b*-PDMS-*b*-PMMA (b) and PMA-*b*-PDMS-*b*-PMA (c) triblocks in the  $\text{CDCl}_3$  solvent.

PDI of terpolymers decrease by increasing conversion (Fig. 5), indicating that ATRP of St, MMA, and MA in the presence of Br-PDMS-Br as macroinitiator proceeds according to the controlled/living characteristic with the well-controlled compositions and molecular weights as well as the narrow polydispersity indices.

DSC thermograms of PDMS homopolymer and PDMS-based triblock copolymers in the temperature

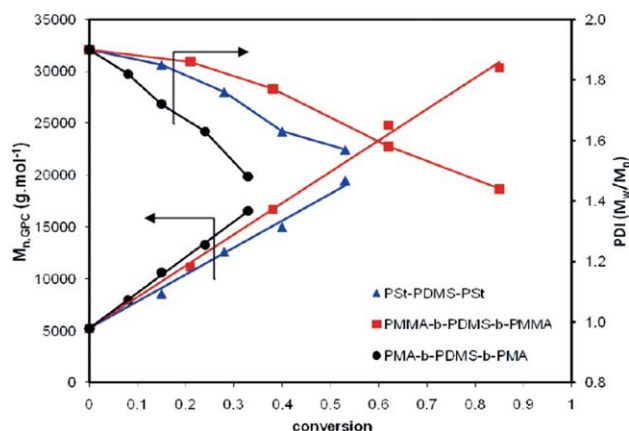


**Figure 4** GPC chromatograms of the Br-PDMS-Br macroinitiator (a) and PSt-PDMS-*b*-PSt triblock copolymer (b).

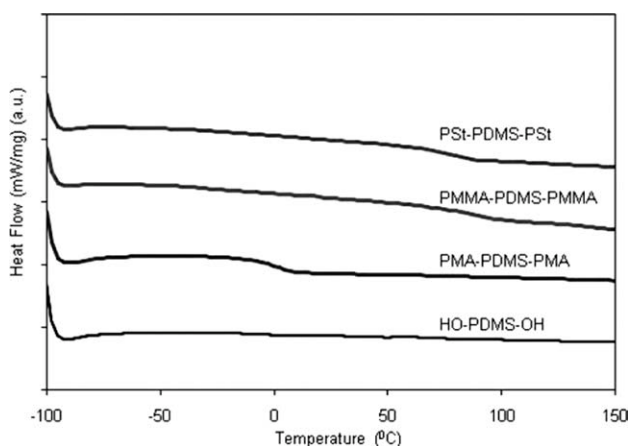
range from  $-100^\circ\text{C}$  to  $+150^\circ\text{C}$  are shown in Figure 6. Glass transition temperature ( $T_g$ ) of PDMS cannot be observed in the Figure 5, because its value has been reported to be about  $-120^\circ\text{C}$ .<sup>28,32,33</sup> PMMA, PSt, and PMA segments in the corresponding triblock copolymers exhibited  $T_g$  values of 89, 83, and  $5^\circ\text{C}$ , respectively (Fig. 6, indicating that  $T_g$  values of PMMA, PSt, and PMA segments are lowered somewhat by the presence of flexible PDMS segment in the center of the terpolymers.<sup>28,40</sup> These results show characteristic of the microphase separated morphology of the triblock copolymers.<sup>28,33</sup> On the basis of DSC results, one can conclude that PDMS-based triblock copolymers have successfully been synthesized.

## CONCLUSION

Poly(dimethylsiloxane)(PDMS)-based triblock copolymers were successfully synthesized via ATRP of St,



**Figure 5** Dependence of experimental number-average molecular weight ( $M_{n,GPC}$ ) and polydispersity index (PDI) of the molecular weight on the monomer conversion for ATRP of the St, MMA, and MA in the presence of Br-PDMS-Br macroinitiator. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]



**Figure 6** DSC thermograms of PDMS homopolymer and PDMS-based triblock copolymers in the temperature range from  $-100^{\circ}\text{C}$  to  $+150^{\circ}\text{C}$  with heating rate of  $10^{\circ}\text{C}/\text{min}$ .

MMA, or MA initiated with bis(bromoalkyl)-terminated PDMS macroinitiator (Br-PDMS-Br) in the presence of  $\text{CuCl}/\text{PMDETA}$  as a catalyst system at  $80^{\circ}\text{C}$ . FTIR,  $^1\text{H}$ NMR and GPC techniques were used to analyze chemical structure of the triblock copolymers. There was a very good agreement between the number-average molecular weight calculated from  $^1\text{H}$ NMR spectra and that calculated theoretically. Also, GPC results showed the narrow polydispersity indices ( $\text{PDI} < 1.57$ ) for the synthesized triblock copolymers which was lower than that of initial macroinitiator ( $\text{PDI} = 1.90$ ), indicating the living/controlled characteristic of the reaction. The results showed that ATRP of St, MMA, and MA in the presence of Br-PDMS-Br as macroinitiator proceeds with the well-controlled compositions and molecular weights as well as the narrow polydispersity indices. DSC results showed that the PDMS-based triblock copolymers exhibit two glass transition temperatures, one corresponding to the  $T_g$  of PDMS segment and other corresponding to the  $T_g$  of PMMA, PMA or PSi segments, indicating characteristic of the microphase separated morphology of the triblock copolymers.

## References

- Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem Rev* 2001, 101, 3689.
- Matyjaszewski, K.; Xia, J. *Chem Rev* 2001, 101, 2921.
- Ibrahim, K. A.; Al-Muhtaseb, A. H.; Seppala, J. *Polym Int* 2009, 58, 927.
- Matyjaszewski, K.; Xia, J. *Chem Rev* 2001, 101, 2921.
- Noda, T.; Grice, A. J.; Levere, M. E.; Haddleton, D. M. *Eur Polym J* 2007, 43, 2321.
- Lian, K. J.; Chen, C. Q.; Liu, H.; Wang, N. X.; Yu, H. J.; Luo, Z. H. *J Appl Polym Sci* 2011, 120, 156.
- Vidts, K. R. M.; Dervaux, B.; Du Prez, F. E. *Polymer* 2006, 47, 6028.
- Medel, S.; Garcia, J. M.; Garrido, L.; Garrido, I. Q.; Paris, R. *J Polym Sci, Part A: Polym Chem* 2011, 49, 690.
- Owen, M. J. *Chimie nouvelle* 2004, 85, 27.
- Kumar, R. C.; Andrus, M. H.; Dueltgen, R. R.; Mazuek, M. H. *ACS Polym Prepr* 1994, 35, 786.
- Shinoda, H.; Matyjaszewski, K.; Okrasa, L.; Mierzwa, M.; Pakula, T. *Macromolecules* 2003, 36, 4772.
- Shinoda, H.; Miller, P. J.; Matyjaszewski, K. *Macromolecules* 2001, 34, 3186.
- Shinoda, H.; Matyjaszewski, K. *Macromol Rapid Commun* 2001, 22, 1176.
- Owen, M. J.; Zeigler, J. M.; Fearon, F. W. G. *J Am Chem Soc* 1990, 224, 705.
- Clarson, S. J.; Semlyen, J. A. *Siloxane Polymers*; Ellis Horwood PTR Prentice Hall Press: New York, 1993.
- Allcock, H. R. *Adv Mater* 1994, 6, 106.
- Matsumoto, N. *J Appl Phys* 1998, 37, 5425.
- Miller, R. D.; Michl, J. *Chem Rev* 1989, 89, 1359.
- Canelas, D. A.; DeSimone, J. M. *Macromolecules* 1997, 30, 5673.
- Harrison, K. L.; Da Rocha, S. R. P.; Yates, M. Z.; Johnston, K. P.; Canelas, D.; DeSimone, J. M. *Langmuir* 1998, 14, 6855.
- Crivello, J. V.; Conlon, D. A.; Lee, J. L. *J Polym Sci, Polym Chem Ed* 1986, 24, 1197.
- Crivello, J. V.; Lee, J. L.; Conlon, D. A. *J Polym Sci, Polym Chem Ed* 1986, 24, 1251.
- Nair, C. P. R.; Clouet, G. *Macromolecules* 1990, 23, 1361.
- Harabagiu, V.; Hamciuc, V.; Giurgiu, D. *Makromol Chem, Rapid Commun* 1990, 11, 433.
- Nakagawa, Y.; Miller, P. J.; Matyjaszewski, K. *Polymer* 1998, 39, 5163.
- Matyjaszewski, K.; Miller, P. J.; Fossum, E.; Nakagawa, Y. *Appl Organometal Chem* 1998, 12, 667.
- Miller, P. J.; Matyjaszewski, K. *Macromolecules* 1999, 32, 8760.
- Brown, D. A.; Price, G. J. *Polymer* 2001, 42, 4767.
- Limer, A.; Haddleton, D. M. *Macromolecules* 2006, 39, 1353.
- Peng, H.; Cheng, S.; Fen, L.; Fan, Z. *Polymer Int* 2004, 53, 833.
- Peng, H.; Cheng, S.; Fan, Z. *J Appl Polym Sci* 2004, 92, 3764.
- Peng, H.; Cheng, S.; Fan, Z. *J Appl Polym Sci* 2004, 92, 532.
- Luo, Z. H.; Yu, H. J.; He, T. Y. *J Appl Polym Sci* 2008, 108, 1201.
- Duquesne, E.; Habimana, J.; Degee, P.; Dubois, P. *Macromol Chem Phys* 2006, 207, 1116.
- Luo, Z. H.; He, T. Y. *React Funct Polym* 2008, 68, 931.
- Pouget, E.; Tonnar, J.; Eloy, C.; Lacroix-Desmazes, P.; Boutevin, B. *Macromolecules* 2006, 39, 6009.
- Tonnar, J.; Pouget, E.; Lacroix-Desmazes, P.; Boutevin, B. *Eur Polym J* 2008, 44, 318.
- Duo, Q.; Wang, C.; Cheng, C.; Han, W.; Thune, P. C.; Ming, W. *Macromol Chem Phys* 2006, 207, 2170.
- Gelstest Catalog, *Reactive Silicones: Forging New Polymer Links*, Gelstest Inc., Morrisville, Pennsylvania 19067, Available at: [www.gelstest.com/company/pdfs/reactivesilicones.pdf](http://www.gelstest.com/company/pdfs/reactivesilicones.pdf).
- Andrews, R. J.; Grulke, E.A. In *Polymer Handbook*, 4th ed.; Brandrup, J.; Immergut, E.H.; Grulke, A.E., Eds.; Wiley: New York, 1999; p VI/193.