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Thereof**

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polyisobutylene (PIB); PMMA; quasiliving ATRP; nanophase separation

**Running Head:** PMMA-PPEGMA-PIB-PPEGMA-PMMA block copolymers

## Abstract

Novel, unique amphiphilic pentablock terpolymers consisting of the highly hydrophobic polyisobutylene (PIB) mid-segment attached to the hydrophilic combshaped poly(poly(ethylene glycol) methacrylate) (PPEGMA) polymacromonomer chains, which are coupled to poly(methyl methacrylate) (PMMA) outer segments were synthesized by the combination of quasiling carbocationic polymerization and atom transfer radical polymerization (ATRP). First, a bifunctional PIB macroinitiator was prepared by quasiling carbocationic polymerization and subsequent quantitative chain end derivatizations. ATRP of PEGMAs with different molecular weights ( $M_n = 188, 300$  and  $475$  g/mol) led to triblock copolymers which were further reacted with MMA under ATRP conditions to obtain PMMA-PPEGMA-PIB-PPEGMA-PMMA ABCBA-type pentablock copolymers. It was found that slow initiation takes place between the PIB macroinitiator and PEGMA macromonomers with higher molecular weights via ATRP. ATRP of MMA with the resulting block copolymers composed of PIB and PPEGMA chain segments led to the desired block copolymers with high initiating efficiency. Investigations of the resulting pentablock copolymers by DSC, SAXS and phase mode AFM revealed that nanophase separation occurs in these new macromolecular structures with average domain distances of 11-14 nm, and local lamellar self-assembly takes place in the pentablocks with PPEGMA polymacromonomer segments of PEGMAs with  $M_n$  of 118 g/mol and 300 g/mol, while disordered nanophases are observed in the block copolymer with PEGMA having molecular weight of 475 g/mol. These new amphiphilic block copolymers composed of biocompatible chain segments can find applications in a variety of advanced fields.

## 1. Introduction

There is significant interest in both academia and industry in multicomponent macromolecular structures composed of covalently bonded well-defined polymer segments with different philicities. The hydrophilic, thermoresponsive poly(poly(ethylene glycol) methacrylate or acrylate) (PPEGMA or PPEGA) combshaped polymacromonomers and the fully saturated, highly hydrophobic, chemically inert and stable, rubbery polyisobutylene (PIB) are among such macromolecules, which have received broad worldwide attention in recent years (see e.g. Refs. 1-29 and references therein). In addition to their interesting physico-chemical properties, it is of special importance that both polymers possess non-immunogeneity and bio- and blood compatibility (6-17). For all these reasons, it is expected that the integration of these two types of polymer segments into one macromolecule may lead to a variety of new application possibilities. However, the mechanical properties of PIB-PPEGMA block copolymers are not expected to be suitable for many applications, because the glass transition temperatures ( $T_g$ ) of both polymers are below room temperature, and therefore highly viscous materials are supposed to be obtained. Improving the strength of such materials can be achieved by either chemical or physical cross-linking. In the case of chemical cross-links, the chains are covalently bonded to each other to form networks, and such materials requires special handling and processing, while polymers with physical cross-links afford the use of conventional polymer processing techniques. In order to form, physical cross-links between amphiphilic PIB-PPEGMA block copolymers at room temperature, an additional glassy macromolecular segment with  $T_g$  higher than this temperature should be chemically coupled to the ends of the block copolymer. However, such terpolymers containing the hydrophobic PIB and hydrophilic PPEGMA connected to a glassy polymer chain have not been reported yet according to the best of our knowledge.

Undoubtedly, quasiling polymerizations (30,31) proceeding by dynamic equilibria between propagating (living) and non-propagating (non-living) polymer chains are the most suitable processes to prepare well-defined macromolecular architectures. Because PIBs with desired terminal functionalities can be synthesized only by quasiling carbocationic polymerization (31), this polymer was selected as the middle block of the planned terpolymer structure. For coupling PPEGMA to the PIB segment, quasiling atom transfer radical polymerization (ATRP) seems to be the optimal choice due to the versatility of this polymerization method for obtaining designed macromolecules of a large number of vinyl monomers from linear to branched architectures (see e.g. Refs. 34-39 and references therein). Due to the fact that ATRP results in polymers with chain ends suitable for subsequent ATRP of selected monomers, the third block, in our case poly(methyl methacrylate) (PMMA), can presumably also be obtained by this process via the utilization of the PIB-PPEGMA diblock as macroinitiator. Herein, we report on the synthesis of PMMA-PPEGMA-PIB-PPEGMA-PMMA ABCBA pentablock copolymers by the combination of quasiling carbocationic polymerization with ATRP.

## **2. Experimental**

### **2.1. Materials**

Poly(ethylene glycol) methyl ether methacrylate macromonomers with different number average molecular weights (188 (PEGMA<sub>188</sub>), 300 (PEGMA<sub>300</sub>) and 475 g/mol (PEGMA<sub>475</sub>)) were purchased from Sigma-Aldrich and were purified via transmitting through a column filled with neutral Al<sub>2</sub>O<sub>3</sub> before use. Methyl methacrylate (MMA) was distilled over CaH<sub>2</sub> under reduced pressure. Toluene was distilled over sodium. Ascorbic acid, 2-bromoisobutryl bromide, ethyl 2-bromoisobutyrate, 1,1,4,7,10,10-hexamethyl-triethylenetetraamine (HMTETA) was purchased from Sigma-Aldrich and used without purification. CuCl was

purchased from Sigma-Aldrich and was stirred with acetic acid overnight, filtered and washed with abs. ethanol and diethyl ether.

## 2.2. Procedures

The bifunctional, 2-bromoisobutyrate-telechelic polyisobutylene (PIB) macroinitiator was prepared by quasiling carbocationic polymerization using 5-*tert*-butyl-1,3-dicumyl chloride bifunctional initiator, TiCl<sub>4</sub> Lewis acid, N,N,N',N'-tetramethylethylenediamine additive in hexane:dichloromethane 60:40 V/V at -78 °C as described earlier (32,33,40). Briefly, the polymerization was quenched with allyltrimethylsilane resulting in allyl-terminated PIB. The allyl groups were transferred to hydroxyl groups via hydroboration using 9-borabicyclononane (9-BBN) followed by oxidation with H<sub>2</sub>O<sub>2</sub>. The 2-bromoisobutyryl end groups were formed by esterification of the hydroxyl groups with 2-bromoisobutyryl bromide in the presence of N,N-dimethylaminopyridine. The resulting polyisobutylene macroinitiator has functionality of 2.0, M<sub>n</sub> = 4400 g/mol and M<sub>w</sub>/M<sub>n</sub> = 1.04 polydispersity.

The pentablock terpolymers were synthesized by quasiling ATRP using the bifunctional PIB macroinitiator possessing 2-bromoisobutyryl endgroups. The applied reaction conditions are summarized in Table 1. In all reactions, CuCl as catalyst and 1,1,4,7,10,10-hexamethyltriethylenetetraamine (HMTETA) was applied as complexing agent. The initiating endgroup:catalyst:HMTETA ratio was 1:1:1 in all cases. L-ascorbic acid as reducing agent (with L-ascorbic acid:catalyst ratio of 1.5:1) was also added to the reaction mixtures. Toluene was applied as solvent with  $V_{solvent}:m_{macroinitiator+monomer}$  ratio of 2:1 (mL/g). First, the hydrophilic poly(ethylene glycol) methacrylate macromonomers were polymerized by using PIB/PEGMA ratio of 1:1 wt/wt. After the preparation of the PPEGMA-*b*-PIB-*b*-PPEGMA triblock copolymers, ATRP of methyl methacrylate was performed by using the triblock copolymers as macroinitiators. The planned  $m(PMMA):m(PPEGMA):m(PIB)$  weight ratio was

1:1:1 which means 33 wt% PIB. For comparison, PPEGMA homo-polymacromonomers were also prepared by ATRP with ethyl 2-bromoisobutyrate initiator. The reaction temperature was 40 °C in all cases. The polymers were purified by passing their solution in toluene through a column filled with neutral Al<sub>2</sub>O<sub>3</sub> followed by evaporation of the solvent and drying to constant weight at room temperature.

Films were made from the pentablock copolymers by solution casting in the following way: circa 150 mg polymer was dissolved in 1 ml chloroform and the solution was poured into a teflon mould (2 cm x 4 cm). The solvent was slowly evaporated under atmospheric pressure at room temperature, and then the films were dried until constant weight under vacuum at room temperature.

### **2.3. Analysis**

The polymer samples were analyzed by gel permeation chromatography (GPC) equipped by a guard column, three PLgel MixedC columns, Waters 515 PLC pump, Waters 717 Autosampler, Jetstream Column Thermostat and Viscotec Dual detector (refractive index and viscosity detector). GPC measurements were performed by applying THF eluent with 1 ml/min flow rate at 25 °C. The chromatograms were evaluated using calibration made with polystyrene standards of narrow molecular weight distribution. Nuclear magnetic resonance (NMR) spectra were recorded in chloroform-*d* on a Varian VXR 200 MHz spectrometer at room temperature. Differential scanning calorimetry (DSC) measurements were performed on a Mettler TG50 equipment in the -120 °C to +160 °C temperature range with 10 °C/min heating rate under N<sub>2</sub> stream using 18-19 mg of samples. The second heating curves were evaluated. Small-angle X-ray scattering (SAXS) measurements were performed on a modified compact Kratky-type camera with slit collimation. Scattering curves were recorded using a one-dimensional positive sensitive proportional counter, and were corrected for X-ray beam

length effects (i. e. "desmeared"). Phase mode atomic force microscopy (AFM) measurements were carried out with a Digital Instruments Nanoscope III equipment.

### 3. Results and Discussion

For the preparation of the targeted PMMA-PPEGMA-PIB-PPEGMA-PMMA ABCBA pentablock copolymers, first the middle block, 2-bromoisobutyryl-telechelic polyisobutylene bis-macroinitiator was synthesized by quasilingiving carbocationic polymerization of isobutylene with a bifunctional initiator, 5-*tert*-butyl-1,3-dicumyl chloride, followed by quantitative chain end derivatizations. The isobutylene polymerization was quenched with allyltrimethylsilane to yield allyl-telechelic PIB, the hydroboration and subsequent oxidation of which with 9-BBN and hydrogen peroxide, respectively, resulted in hydroxyl-telechelic polymer (32,33). Esterification with 2-bromoisobutyryl bromide led to the desired PIB bis-macroinitiator with 2-bromoisobutyryl termini which are capable to initiate ATRP (40). The resulting PIB macroinitiator with  $M_n = 4400$  g/mol and  $M_w/M_n = 1.04$  has functionality of 2.0 as the integration ratio of the  $^1\text{H}$  NMR signals of the initiator moiety at 7.17 ppm and the  $-\text{CH}_2-$  protons of the terminal ester groups at 4.14 ppm indicates (see the  $^1\text{H}$  NMR spectrum in Figure 1).

In the next step, ATRP of PEGMA macromonomers with molecular weights of 188 g/mol (PEGMA<sub>188</sub>), 300 g/mol (PEGMA<sub>300</sub>) and 475 g/mol (PEGMA<sub>475</sub>) were attempted by using the PIB macroinitiator in conjunction with the CuCl/HMTETA catalyst system in toluene at 40 °C as shown in Scheme 1. In all cases, the PIB/PEGMA weight ratios were 50/50, and high macromonomer conversions (96-99%) were observed under the applied conditions. This is confirmed by the  $^1\text{H}$  NMR spectra of the resulting PIB-PPEGMA block copolymers, in which negligible signals can be detected at 5.55 and 6.11 ppm characteristic for the olefinic protons of the unreacted PEGMA macromonomers (Figure 2). As the GPC curves indicate in Figure



3, there is a shoulder in the lower molecular weight region, the intensity of which increases with the molecular weight of PPEGMA, i. e. it is negligible with the PEGMA<sub>188</sub> and more pronounced in the case of PEGMA<sub>475</sub>. This indicates that steric hindrance between the PIB macroinitiator and PEGMA macromonomer results in slow initiation, and diblock copolymers may also be present in the resulting block copolymers. However, nearly perfect triblock copolymers can be obtained with PEGMA<sub>188</sub> possessing the lowest molecular weight among the investigated macromonomers. This means that unique block copolymers which are composed of the highly hydrophobic polyisobutylene as mid-segment and the combshaped, hydrophilic poly(poly(ethylene glycol) methacrylate) polymacromonomer as outer segments can be obtained by ATRP of PEGMA macromonomers initiated by the PIB macroinitiator. The formation of block copolymers is also evident from the  $M_n$  values in Table 2, which indicates doubling of the molecular weight according to the nearly complete macromonomer conversion. At the same time, the molecular weight distribution remains fairly narrow with polydispersity indices ( $M_w/M_n$ ) in the range of 1.22-1.39 as a consequence of the quasiling ATRP of the PEGMA macromonomers.

Taking into account that the resulting PIB-PEGMA block copolymers bear halogen termini capable to initiate further ATRP as macroinitiators, polymerization of methyl methacrylate (MMA) was carried out to form pentablock copolymers as displayed in Scheme 1. For this step, MMA was selected because PMMA is a glassy polymer at room temperature since it has  $T_g$  in the range of 100 °C, while the  $T_g$ s of both PIB and PPEGMA polymacromonomers are well below 0 °C as shown in Figure 4 and in Table 3. As a consequence, the block copolymers consisting of PIB and PPEGMA segments are highly viscous materials at room temperature, that is, these materials possess poor mechanical properties for several potential applications. In order to obtain mechanically stable materials, it is expected that PMMA segments coupled to the PIB-PPEGMA block copolymers form

physical cross-links, and thus improve the properties of these materials at room temperature. Another aspect of selecting MMA is due to the fact that it has similar structure to the PEGMA macromonomers, and it can be polymerized by ATRP (see e.g. Refs. 34-37,41-43 and references therein). In these experiments, the weight ratio of PIB was selected to be 33 wt%, and thus the formation of pentablock copolymer systems with 1:1:1 PIB:PPEGMA:PMMA composition are expected in cases of nearly complete MMA conversion. As shown in Figures 3 and 5, the polymerization of MMA led to block copolymers with near to 100% MMA conversions. The  $^1\text{H}$  NMR spectrum in Figure 5 clearly indicates the absence of unreacted MMA, that is, the complete consumption of this monomer in the applied process. The GPC traces in Figure 3 show that there is significant and uniform shift toward lower elution volumes, i. e. toward higher molecular weights, upon MMA polymerization. The  $M_n$  values in Table 2 also corroborate this observation, because the molecular weights increased with near to the expected 4440 g/mol. The polydispersity indices fall between 1.23-1.49, that is there is no significant broadening upon MMA polymerization. This means efficient block copolymer formation under the applied polymerization conditions. It has to be noted that the films prepared from the obtained pentablock copolymers meet our expectations, and are indeed mechanically strong enough to handle. It is also observed that longer the poly(ethylene glycol) side chains, softer the materials.

The resulting pentablock copolymers were characterized by DSC, SAXS and phase mode AFM. As the results of the DSC analysis indicate in Figure 5 and Table 3, the PIB macroinitiator has a  $T_g$  at  $-63.8\text{ }^\circ\text{C}$ , while the PPEGMA<sub>188</sub>, PPEGMA<sub>300</sub> and PPEGMA<sub>475</sub> polymacromonomers at  $-41.0\text{ }^\circ\text{C}$ ,  $-56.1\text{ }^\circ\text{C}$  and  $-62.8\text{ }^\circ\text{C}$ , respectively that is with the exception of PPEGMA<sub>188</sub> close to that of the PIB. The DSC curve of the PPEGMA<sub>475</sub> shows that this polymacromonomer is a semicrystalline material with melting temperature of  $-1.5\text{ }^\circ\text{C}$ . On the basis of the enthalpy of melting of pure poly(ethylene oxide) of 197 J/g (44), the extent of

crystallinity of the PEG side chains of PPEGMA<sub>475</sub> is 20%. It is evident in Figure 4 that the crystallinity of PPEGMA<sub>475</sub> is suppressed in the PPEGMA-PIB-PPEGMA block copolymer, and indeed, it is only 4%. Surprisingly, no crystalline fraction can be observed in the corresponding pentablock copolymer. This means that coupling PMMA outer blocks to the PIB-PPEGMA<sub>475</sub> block copolymers completely suppresses crystallization of the pendant PEG chains of the PPEGMA<sub>475</sub> polymacromonomer segments. Two glass transitions are observed for the ABA block of the copolymers with the PPEGMA<sub>188</sub> blocks at -58.9 °C for PIB and -37.2 °C for the polymacromonomer, indicating phase separation in this material between the components. Due to the nearly coinciding  $T_g$ s of PIB, PPEGMA<sub>300</sub> and PPEGMA<sub>475</sub> only one glass transition can be seen for the corresponding triblocks in the DSC curves. For the pentablocks containin outer PMMA segments, broad glass transitions are observed in every case by DSC. Two glass transition temperatures are observed for sample 6 with PPEGMA<sub>475</sub> as second block at -55.6 °C and -37.1 °C indicating phase separation in this block copolymer. Interestingly, the glass transition of the PMMA segments cannot be detected in these materials by DSC. This can be due to the relatively low average molecular weight of the PMMA (~2200 g/mol) and/or to its partial miscibility with the PPEGMA chains which may lead to plasticizing effect and thus significant broadening of the glass transition of PMMA, not allowing its detection by DSC.

In order to obtain information on the morphology of the prepared block copolymers, SAXS and phase mode AFM measurements were performed with solution casted samples. As shown in Figure 6, SAXS curves with distinct maxima ( $q_{max}$ ) are obtained indicating the presence of phase separation of the investigated pentablock copolymers with average domain distances of 13.1 nm for samples 4 and 5, and 13.7 nm for sample 6. However, well-defined higher order of self-assembly cannot be seen in the SAXS curves in Figure 6, although a broad shoulder with low intensity can be found at  $2q_{max}$  values which might be due to the

presence of some lamellar arrangements. Indeed, the AFM images confirm this scenario as it is shown in Figure 7. In these images, the bright areas represent the hard, while the dark ones the soft domains. These latter contains mainly PIB and PPEGMA blocks, the hard domains are mostly composed of the glassy PMMA and likely PMMA-PPEGMA mixed phases as well. Lamellar local self-assembly with changing orientation can be seen in the cases of the pentablocks containing PPEGMA<sub>188</sub> (sample 4) and PPEGMA<sub>300</sub> (sample 5) with average domain distances of 12.1 nm and 10.7 nm, respectively. These data fit quite well with that of obtained by SAXS, i. e. 13.1 nm domain distances for these samples. For the block copolymer with PPEGMA<sub>475</sub> (sample 6) a largely disordered domain structure is obtained by AFM. These data indicate that the block copolymers consisting of PIB, PPEGMA and PMMA chain segments, obtained by successive quasiling carbocationic polymerization and a two-step ATRP, are nanophase separated materials with hard and soft domains in the range of 5-10 nm.

#### **4. Conclusions**

The synthesis of amphiphilic ABCBA pentablock terpolymers consisting of the hydrophobic polyisobutylene (C), the hydrophilic poly(poly(ethylene glycol) methacrylate) polymacromonomer (B) and poly(methyl methacrylate (A) chain segments. After successful synthesis of bifunctional PIB macroinitiator by quasiling carbocationic polymerization of isobutylene followed by subsequent chain end derivatizations, triblock copolymers via quasiling ATRP of PEGMAs were prepared. It was found that with increasing molecular weight of the PEGMA macromonomers, slow initiation occurs by the PIB macroinitiator which is due to the steric hindrance between the macroinitiator and the macromonomer. However, subsequent ATRP of MMA with the triblock macroinitiators led to polymerization with high efficiency and block copolymers with expected molecular weight were formed. DSC, SAXS and AFM measurements revealed that phase separation occurs in these block

copolymers with hydrophilic and hydrophobic segments at the nanoscale resulting in average domain sizes between 5-10 nm. These new, nanophase separated pentablock copolymers may find applications in several advanced areas from biomaterials to specialty non-ionic surfactants etc.

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**Table 1.** The macroinitiator, the applied monomer and the PIB content in the feed for quasiliving ATRP of PEGMA and MMA with the CuCl/HMTETA catalyst system (solvent: toluene, 40 °C, 3 days reaction time).

<b>Sample</b>	<b>Macroinitiator</b>	<b>Monomer</b>	<b>PIB wt% in the feed</b>
1	PIB	PEGMA <sub>188</sub>	50
2	PIB	PEGMA <sub>300</sub>	50
3	PIB	PEGMA <sub>475</sub>	50
4	PPEGMA <sub>188</sub> - <i>b</i> -PIB- <i>b</i> -PPEGMA <sub>188</sub>	MMA	33
5	PPEGMA <sub>300</sub> - <i>b</i> -PIB- <i>b</i> -PPEGMA <sub>300</sub>	MMA	33
6	PPEGMA <sub>475</sub> - <i>b</i> -PIB- <i>b</i> -PPEGMA <sub>475</sub>	MMA	33



**Table 2.** The number average molecular weights ( $M_n$ ) and polydispersity ( $M_w/M_n$ ) values of the PIB macroinitiator, the ABA block copolymers (samples 1-3) and the pentablocks (samples 4-6) obtained by the evaluation of the GPC chromatograms (sample identification as in Table 1).

<b>Sample</b>	<b><math>M_n</math></b>	<b><math>M_w/M_n</math></b>
PIB	4400	1.04
1	9100	1.35
2	9000	1.39
3	8000	1.22
4	13900	1.37
5	13200	1.49
6	12600	1.23

**Table 3.** The glass transition temperatures ( $T_g$ ) of the PIB macroinitiator, the PEGMA macromonomers and the synthesized block copolymers, and the observed melting temperatures ( $T_m$ ).

<b>Sample</b>	<b><math>T_g / ^\circ\text{C}</math></b>		<b><math>T_m / ^\circ\text{C}</math></b>
PIB	-63.8		
PPEGMA <sub>188</sub>	-41.0		
PPEGMA <sub>300</sub>	-56.1		
PPEGMA <sub>475</sub>	-62.8		-1.7
1	-58.9	-37.2	
2	-59.0		
3	-61.8		0.3
4	-56.5		
5	-55.7		
6	-55.0	-37.1	

## SCHEME AND FIGURE CAPTIONS

**Scheme 1.** The synthetic route of the preparation of PMMA-PPEGMA-PIB-PPEGMA-PMMA ABCBA-type pentablock copolymers.

**Figure 1.** The  $^1\text{H}$  NMR spectrum of the 2-isobutyryl-telechelic polyisobutylene macroinitiator.

**Figure 2.** The  $^1\text{H}$  NMR spectrum of the reaction mixture at the end of the polymerization of the PEGMA<sub>188</sub> macromonomer by quasiliving ATRP (sample 1 in Table 1).

**Figure 3.** Gel permeation chromatograms of the PIB macroinitiator and the synthesized block copolymers (sample identification as in Table 1).

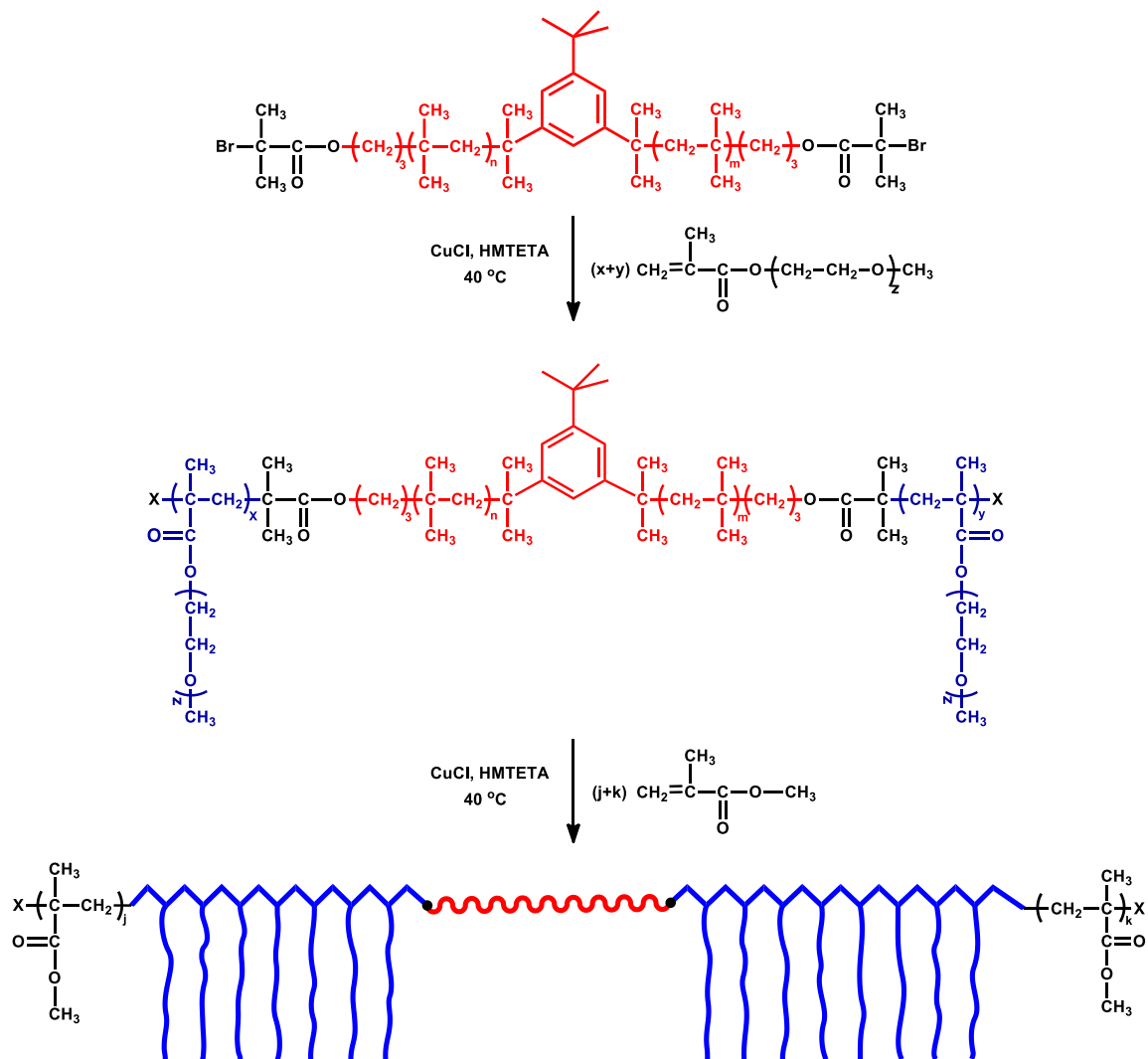
**Figure 4.** The  $^1\text{H}$  NMR spectrum of the reaction mixture at the end of MMA polymerization (sample 4 in Table 1).

**Figure 5.** Differential scanning calorimetry (DSC) curves of the PIB macroinitiator, the PEGMA macromonomers and the synthesized block copolymers.

**Figure 6.** Small angle X-ray scattering (SAXS) curves of the pentablock terpolymers (sample identification as in Table 1).

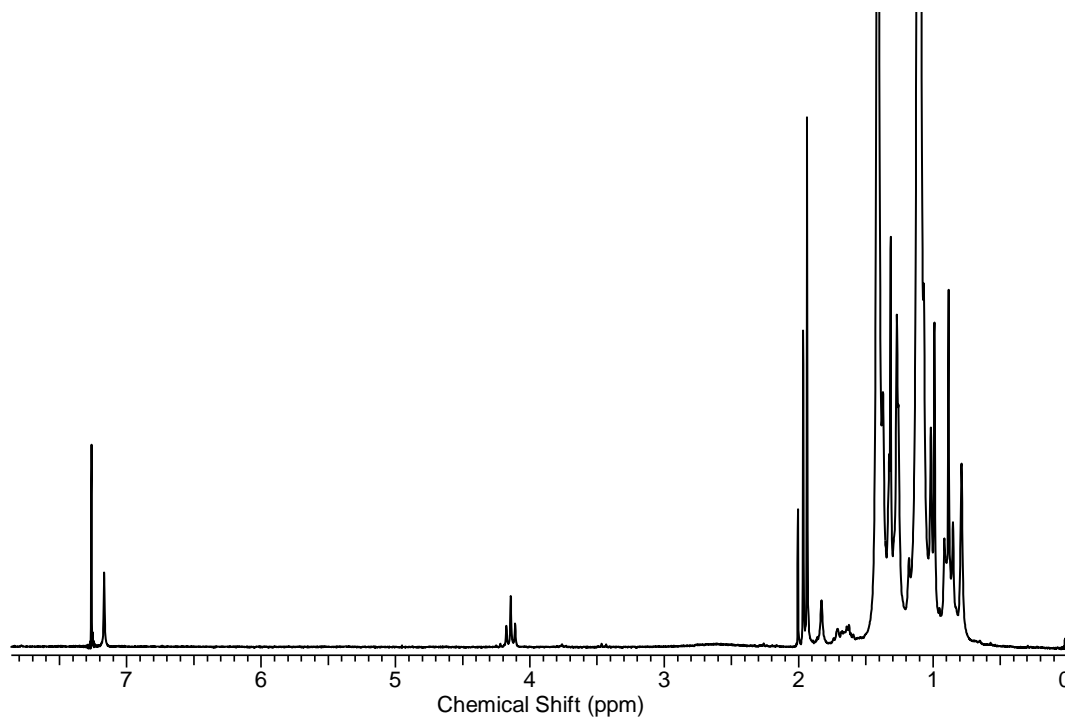
**Figure 7.** Phase-mode atomic force microscopy (AFM) images of the pentablock terpolymers (500x500) nm image size; sample identification as in Table 1).

# SCHEME 1

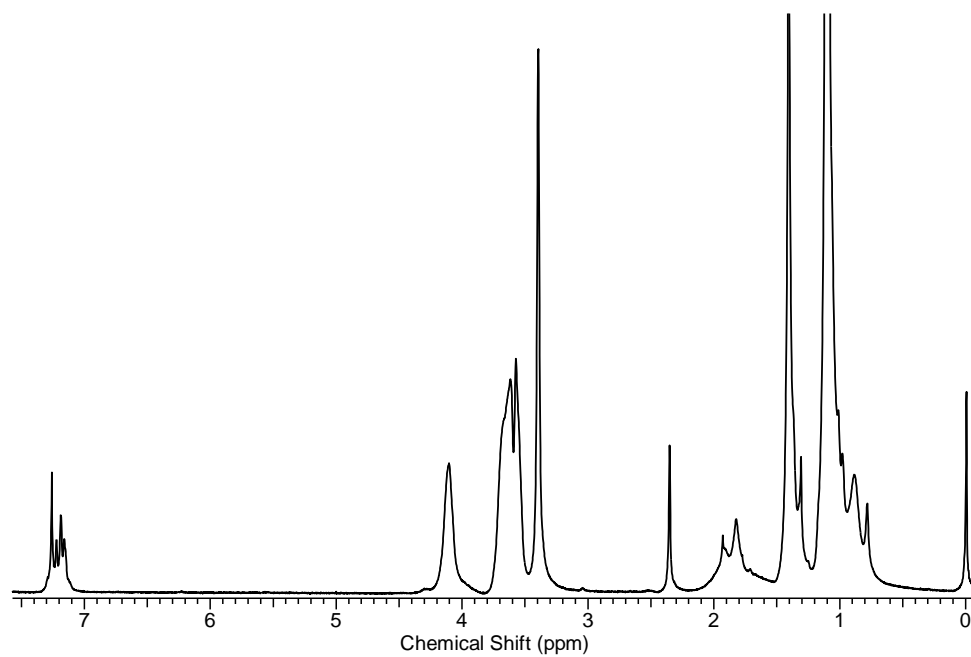


**PMMA-PPEGMA-PIB-PPEGMA-PMMA**

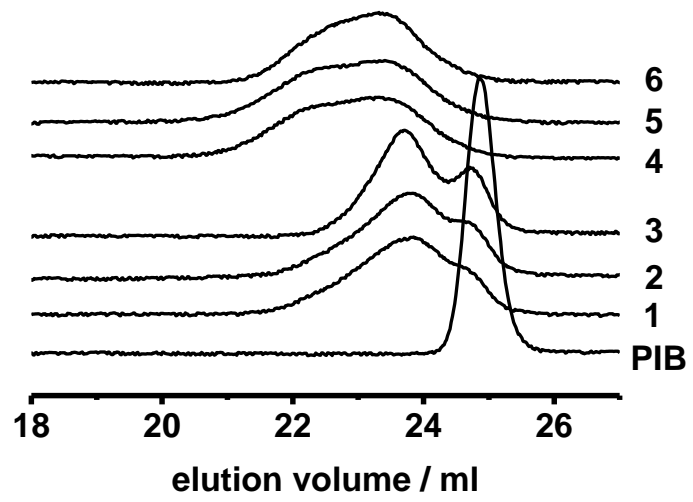
**FIGURE 1**



**FIGURE 2**



**FIGURE 3**



**FIGURE 4**

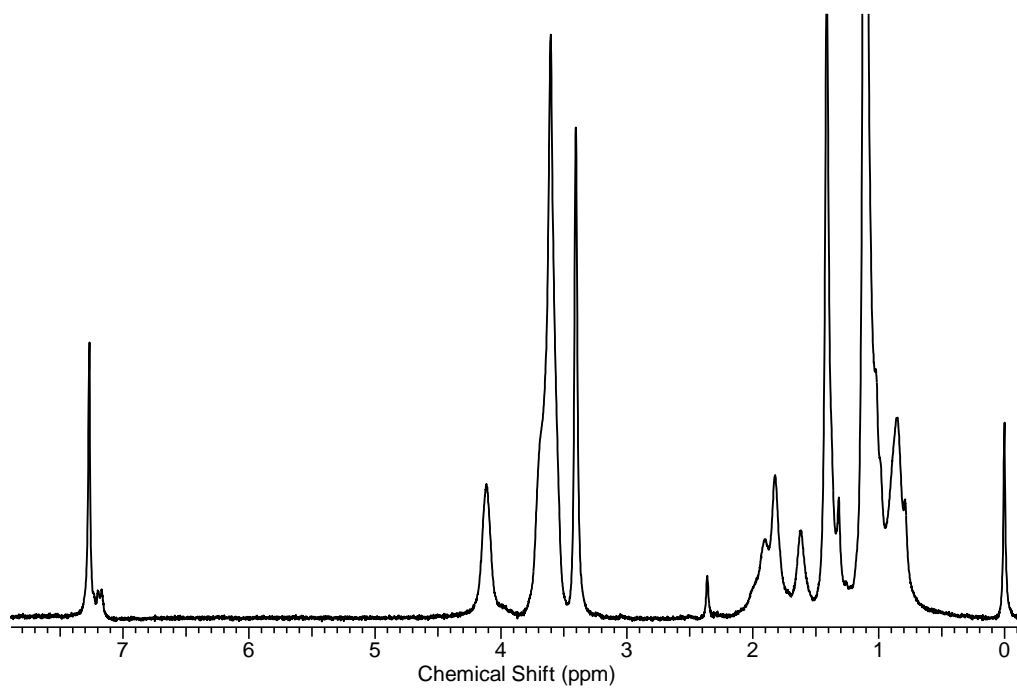




FIGURE 5

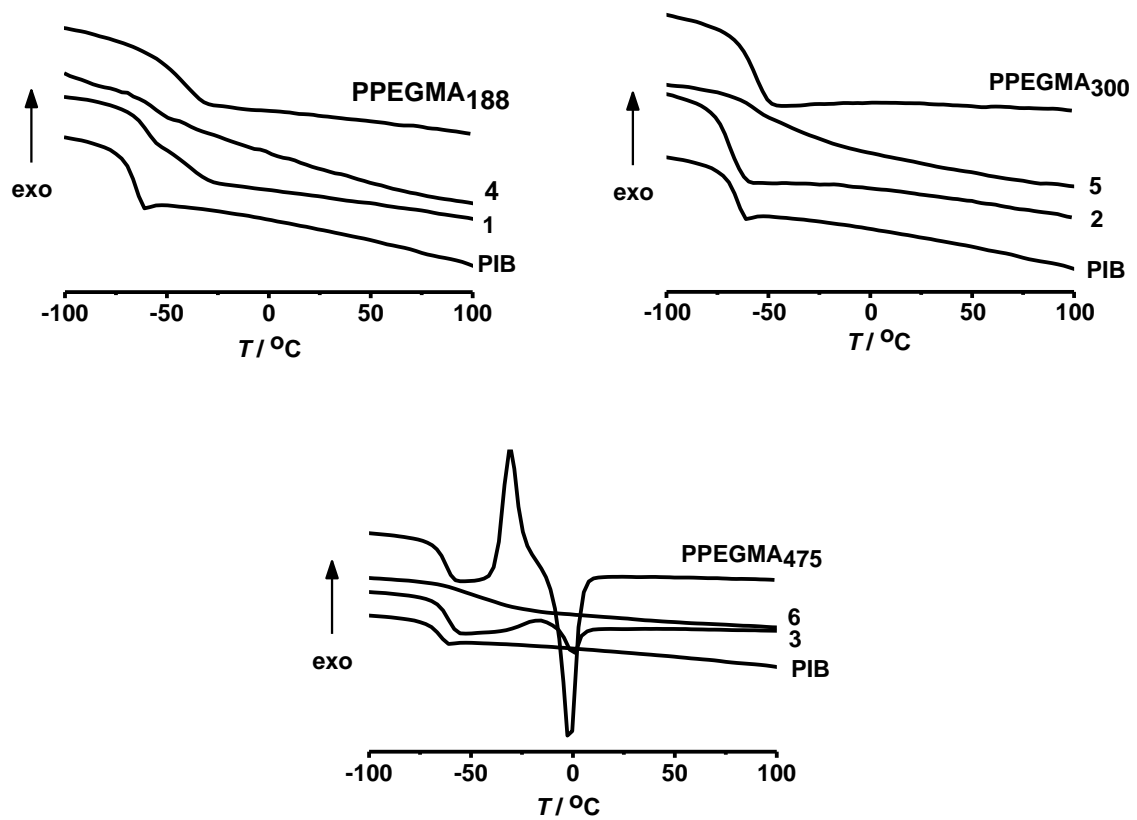
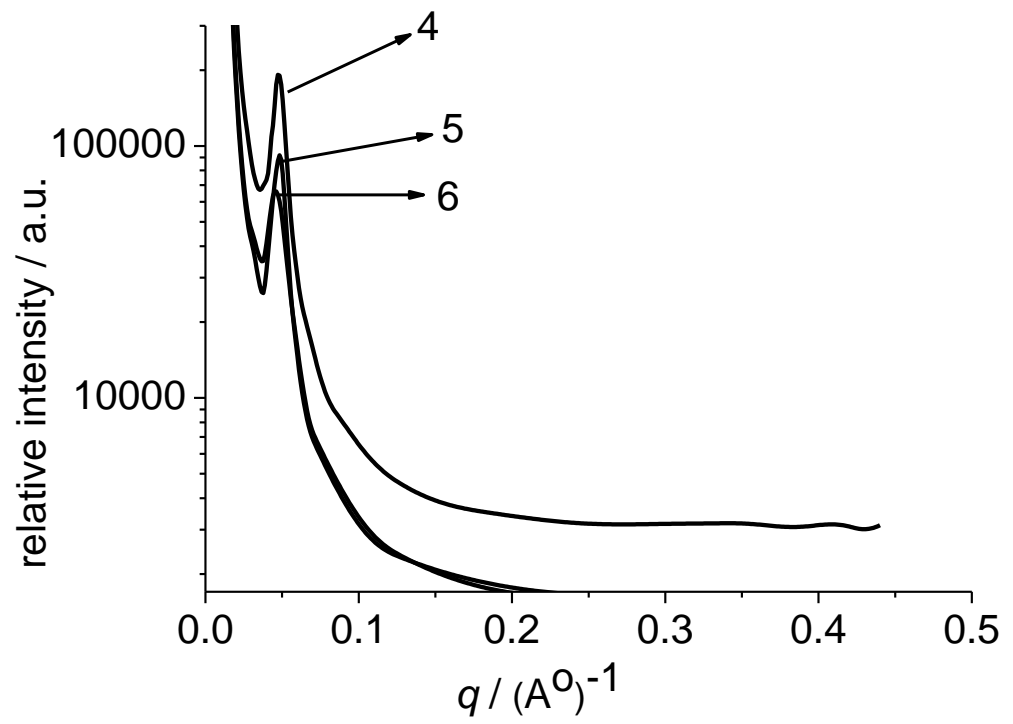
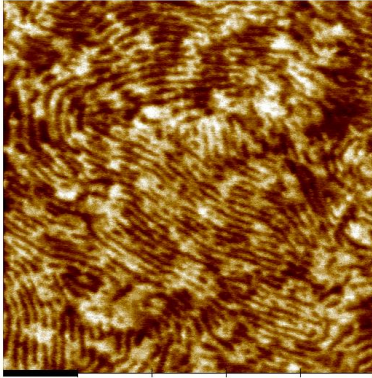


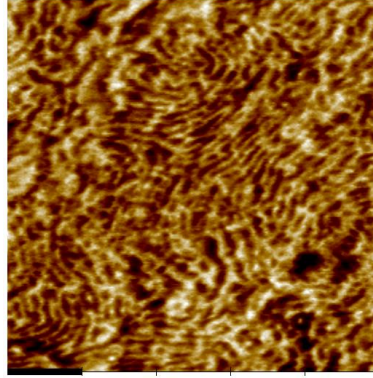
FIGURE 6



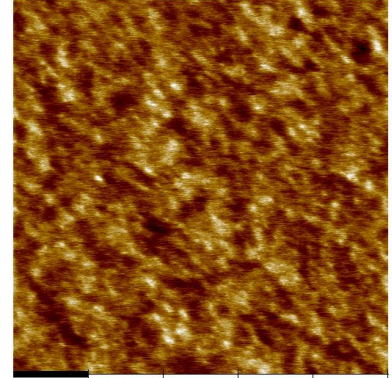
**FIGURE 7**



**Sample 4**



**Sample 5**



**Sample 6**