

## POLYISOBUTYLENE-POLY(POLY(ETHYLENE OXIDE) (METH)ACRYLATE) BLOCK COPOLYMERS AND CONETWORKS

ÁKOS SZABÓ<sup>a,b,\*</sup>, BÉLA IVÁN<sup>a,b</sup>

**ABSTRACT.** In our work, first a telechelic bromoisobutyrate-ended polyisobutylene macroinitiator was synthesized via quasiliving carbocationic polymerization and subsequent chain end modification. In the second step, quasiliving atom transfer radical polymerization (ATRP) of poly(ethylene oxide) methacrylate using the macroinitiator was performed. When ethyleneglycol dimethacrylate was further polymerized on the formed triblock copolymer, a conetwork with a unique structure was obtained.

**Keywords:** polyisobutylene, poly(ethylene oxide)-methacrylate, amphiphilic block copolymers, amphiphilic conetworks, smart polymers

### INTRODUCTION

Hydrophobic polyisobutylene [1] and hydrophilic poly(ethylene oxide) [2] are biocompatible polymers and are applied in therapeutics. However, homopolymers are not appropriate for novel smart medical applications [3]. Therefore, researchers focus on novel smart macromolecular structures which could open new ways in therapeutical technologies [4].

Poly(poly(ethylene oxide) methacrylate)s are water-soluble homopolymers having lower critical solution temperature (LCST) [5] which is tunable with changing the length of the poly(ethylene oxide) side chains [6]. Polymerization of poly(ethylene oxide) methacrylates is performed often by quasiliving atom transfer radical polymerization (ATRP) [5,7,8] which gives well-defined polymer structures. In our work, amphiphilic triblock copolymers composed of hydrophobic polyisobutylene and hydrophilic poly(poly(ethylene oxide) methacrylate) segments were synthesized by ATRP. During these processes 2-bromoisobutyrate-telechelic polyisobutylene macroinitiators were used [9].

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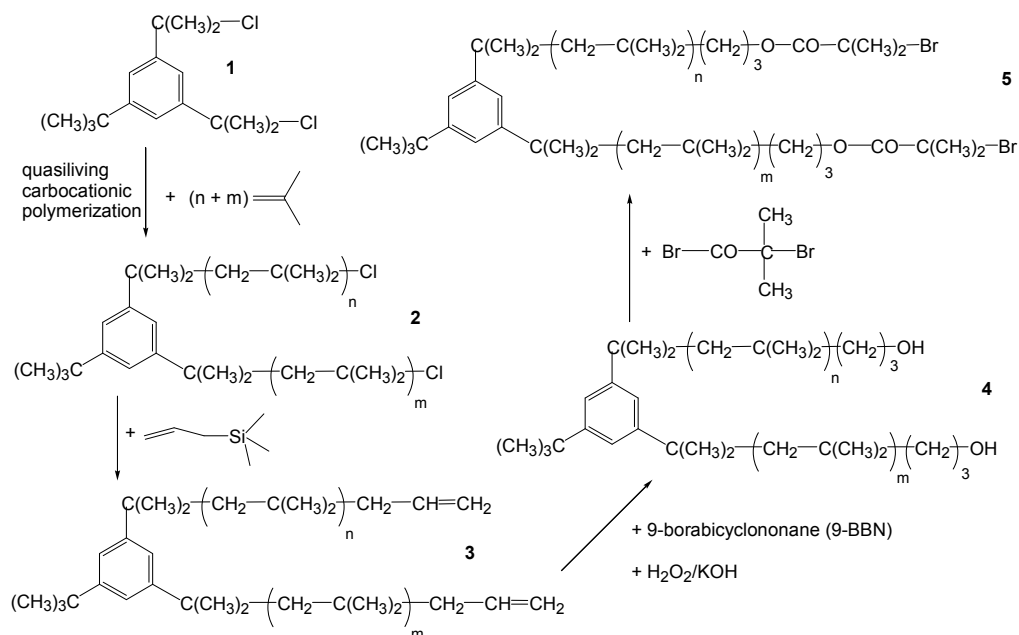
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Amphiphilic conetworks are polymer networks composed of covalently bonded hydrophobic and hydrophilic segments which swell both in polar and non-polar solvents [10]. One of the ways of its synthesis is „endlinking” of block copolymers [11]. The main advantage of these conetworks is the well-defined length of the segments. We also obtained conetworks by endlinking of poly(poly(ethylene oxide) methacrylate)-*b*-polyisobutylene-*b*-poly(poly(ethylene oxide) methacrylate) block copolymers. Previously, such copolymers were synthesized by Janata et al., however, they performed copolymerization of poly(ethylene oxide) methacrylates and methacrylate-telechelic polyisobutylene [12] which does not result in well-defined segment lengths.

## RESULTS AND DISCUSSION

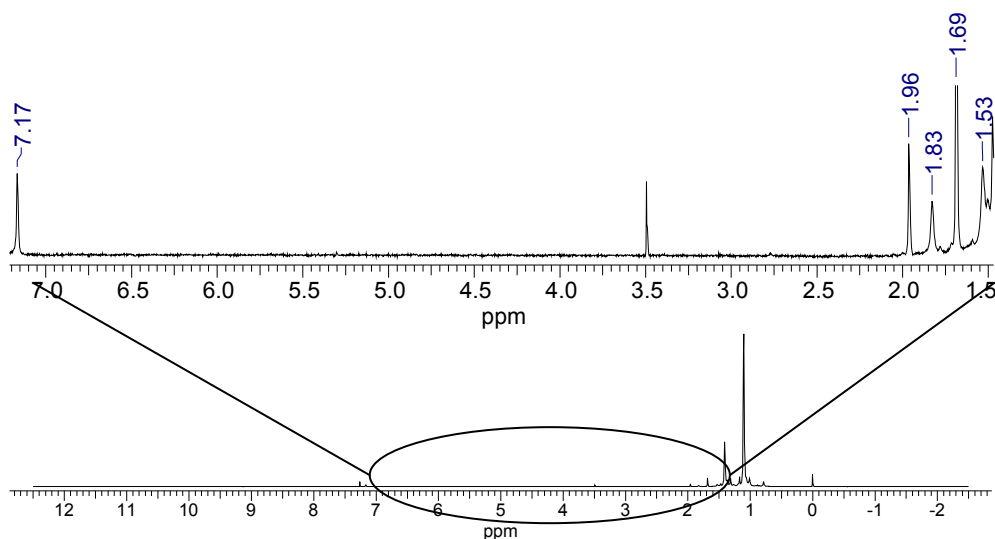
### Synthesis of 2-bromoisobutyrate-telechelic polyisobutylene (5)

ATRP initiator 2-bromoisobutyrate-telechelic polyisobutylene (**5**) was synthesized via quasiliving carbocationic polymerization of isobutylene followed by chain end modification (Scheme 1).

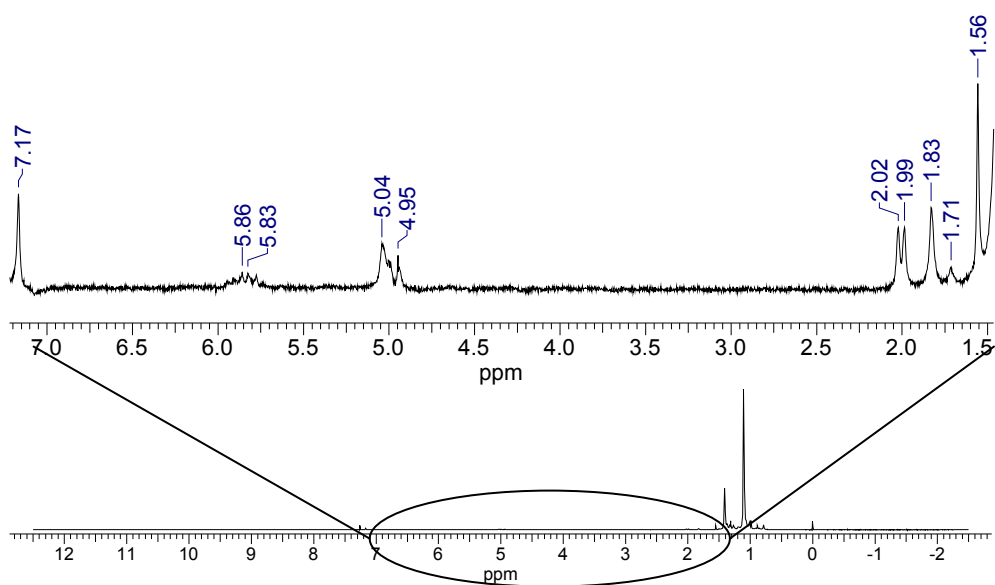


Scheme 1.

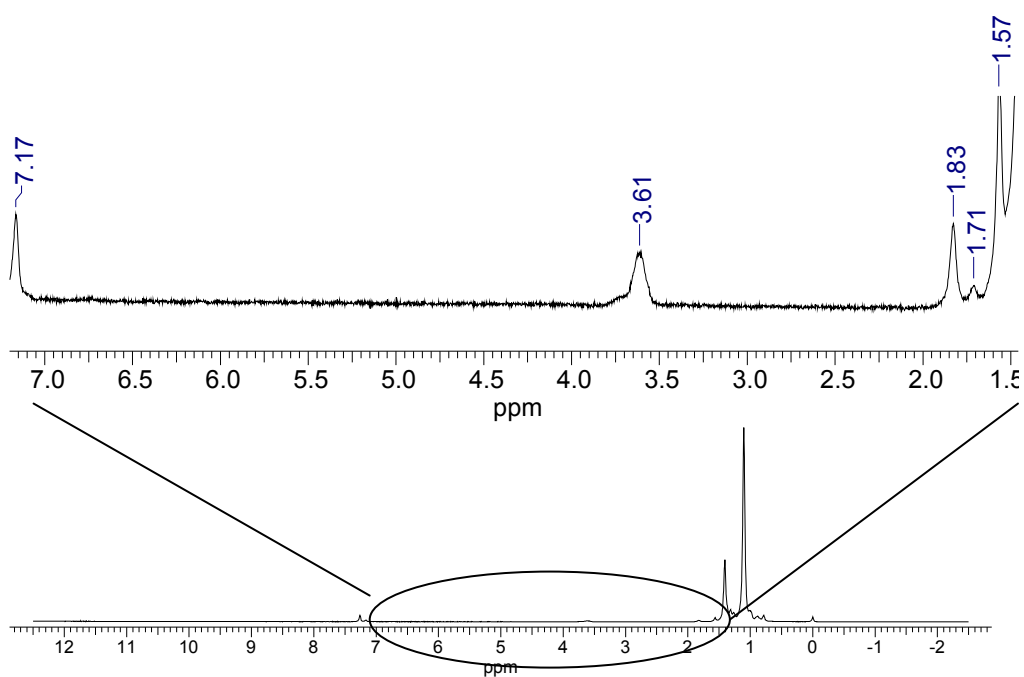
Quasiliving carbocationic polymerization of isobutylene was initiated by the bifunctional initiator 5-*tert*-butyl-1,3-dicumyl-chloride (**1**). Figure 1 shows the  $^1\text{H}$  NMR spectrum of the polyisobutylene ( $M_n = 7500$ ) before the addition of allyl-trimethylsilane (**2**). The peaks of the chloro chain ends appear at 1.69 ppm (methyl groups) and 1.96 ppm (methylene groups). (The peak at 3.49 ppm belongs to methanol residue.) When the chloro-ended polyisobutylene (**2**) was reacted with allyltrimethylsilane under the conditions of the quasiliving carbocationic polymerization [13], allyl-telechelic polyisobutylene (**3**) was formed. The  $^1\text{H}$  NMR spectrum of the allyl-telechelic polyisobutylene (**3**) can be seen in Figure 2. The disappearance of the peaks at 1.69 and 1.96 ppm and the appearance of new peaks at 2.01 ppm, 5.0 ppm and 5.8 ppm confirms that the modification was nearly quantitative. After that, hydroxyl chain ends were synthesized via hydroboration and subsequent oxidizing reaction under alkaline conditions [13]. In the  $^1\text{H}$  NMR spectrum of **4** (Figure 3), the peaks of allylic chain ends disappear and a new peak appears at 3.61 ppm which confirms the nearly quantitative formation of the hydroxyl end groups. In the last step, an esterification was performed with 2-bromoisobutyryl bromide [9]. The disappearance of the peak of hydroxyl end groups and the appearance of a new triplet at 4.14 ppm on the  $^1\text{H}$  NMR spectrum (Figure 4) denotes the nearly quantitative formation of the 2-bromoisobutyrate-telechelic polyisobutylene macroinitiator (**5**). The macroinitiator with 11200 g/mol number average molecular weight was also formed nearly quantitatively by using these reactions.



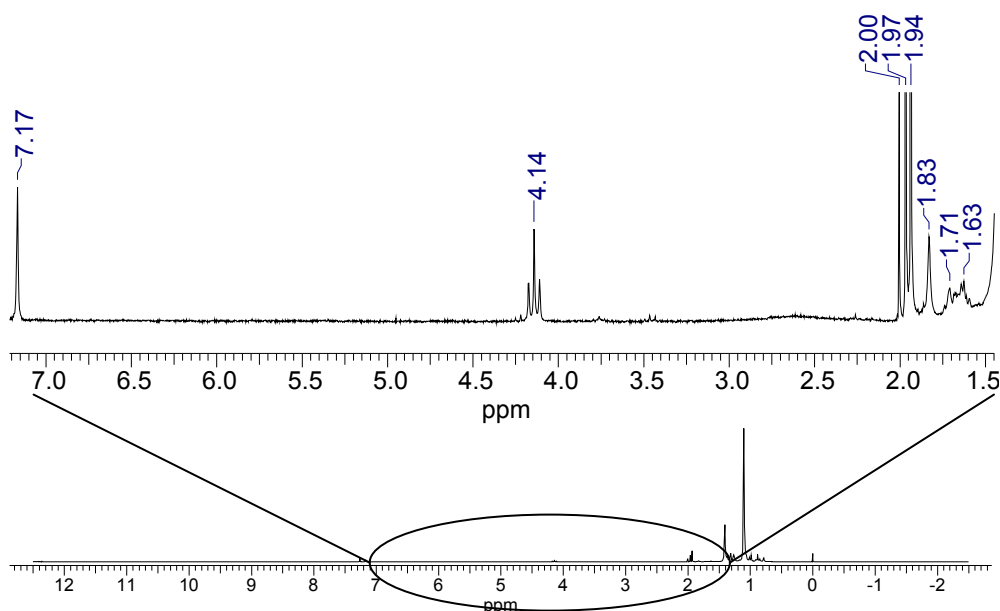
**Figure 1.**  $^1\text{H}$  NMR spectrum of chloro-ended polyisobutylene (**2**) ( $M_n = 7500$  g/mol).



**Figure 2.**  $^1\text{H}$  NMR spectrum of allyl-telechelic polyisobutylene (**3**) ( $M_n = 7500$  g/mol).

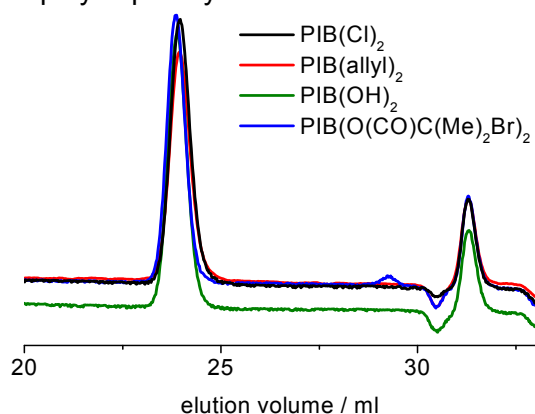


**Figure 3.**  $^1\text{H}$  NMR spectrum of hydroxyl-telechelic polyisobutylene (**4**) ( $M_n = 7500$  g/mol).



**Figure 4.**  $^1\text{H}$  NMR spectrum of 2-bromoisobutyrate-telechelic polyisobutylene (5) ( $M_n = 7500$  g/mol).

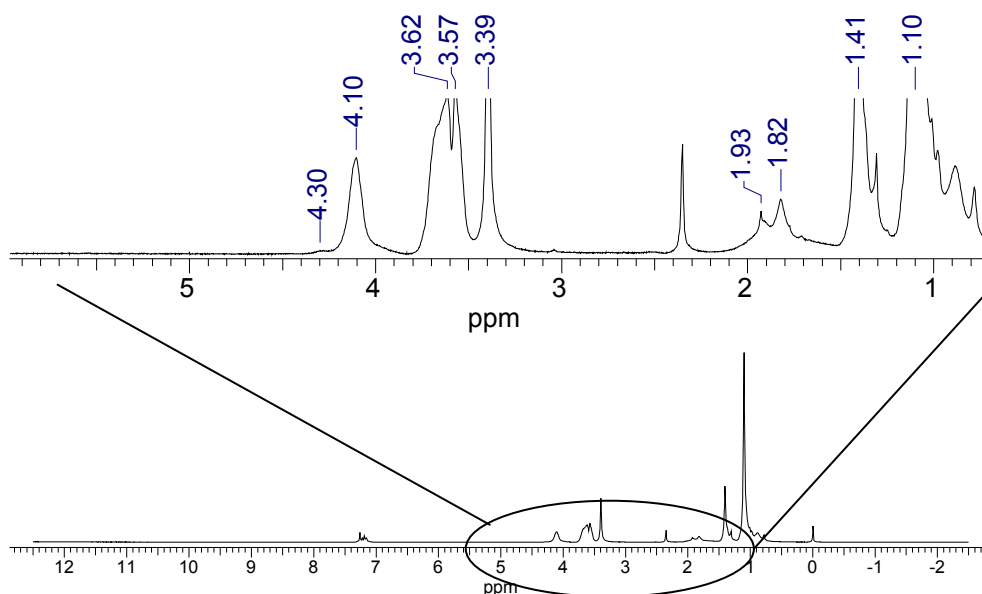
The gel permeation chromatograms of the polyisobutylenes obtained in the different steps (Figure 5) show that the initial narrow molecular weight distribution do not change during the different chain end modification reactions since one monomodal peak at same elution volume could be observed in all cases. The measured molecular weight of this polyisobutylene macroinitiator was 7500 g/mol, its polydispersity index was 1.09.



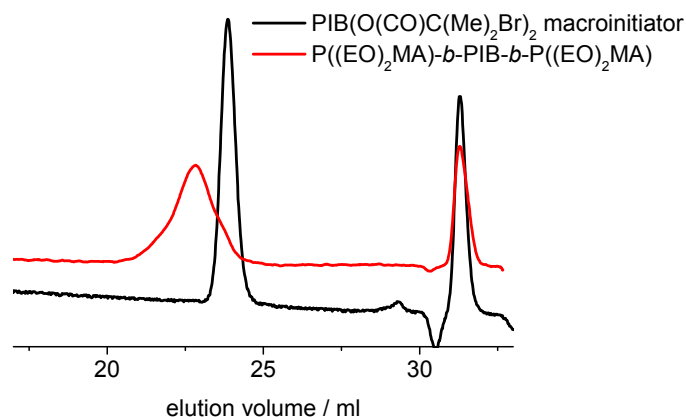
**Figure 5.** Gel permeation chromatograms of polyisobutylenes ( $M_n = 7500$ ) obtained in the different steps of chain-end modification.

### *Synthesis of the amphiphilic triblock copolymer*

Quasiliving atom transfer radical polymerization (ATRP) of di(ethylene oxide)-methacrylate initiated by 2-bromoisobutyrate-telechelic polyisobutylene (**5**) was performed. The conversion was calculated on the basis of the  $^1\text{H}$ -NMR spectrum of the reaction mixture (Figure 6) taken at the end of the reaction since the chemical shift of the  $-\text{COOCH}_2-$  groups of di(ethylene oxide)-methacrylate differs in the case of free monomer molecules (4.30 ppm) and polymerized monomeric units (4.10 ppm). These data indicate that 98% conversion was reached when CuCl was used as catalyst and toluene as solvent at 40 °C after 94 h reaction time. The characteristic peak of the macroinitiator at 4.14 ppm is invisible in the  $^1\text{H}$ -NMR spectrum (Figure 6) which indicates that the initiator efficiency was also near to 100%. The gel permeation chromatogram (Figure 7) confirms this, since the peak shifts to the lower elution volumes as a consequence of the polymerization indicates the increase of the molecular weight of most of the chains. The formed amphiphilic triblock copolymer was not water soluble.



**Figure 6.**  $^1\text{H}$  NMR spectrum of the reaction mixture at the end of the poly(ethylene oxide)-methacrylate polymerization initiated by 2-bromoisobutyrate-telechelic polyisobutylene.



**Figure 7.** Gel permeation chromatogram of  $P((EO)_2MA)-b-PIB-b-P((EO)_2MA)$  triblock copolymer.

#### *Synthesis of amphiphilic conetworks via ATRP*

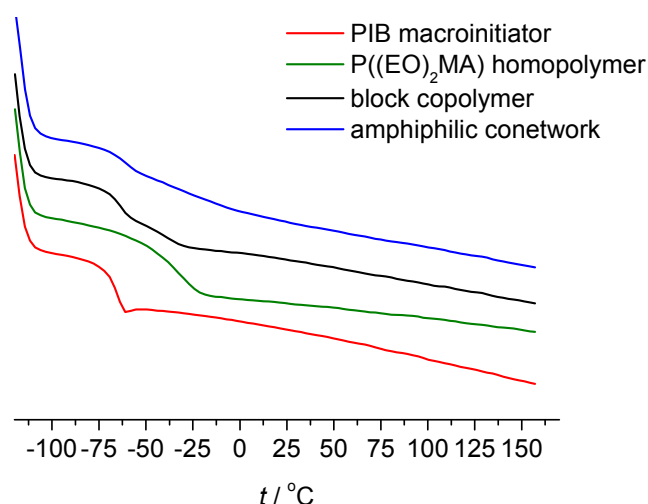
One of the important features of the living polymerizations is that the formed polymer is able to initiate subsequent polymerization with the same mechanism as it was produced with. So, the  $P((EO)_2MA)-b-PIB-b-P((EO)_2MA)$  block copolymer can also act as macroinitiator in ATRP processes. The bifunctional monomer ethyleneglycol dimethacrylate (EGDMA) was polymerized with this block copolymer as macroinitiator. The product was a gel (Figure 8) which was not soluble in any solvent (water, hexane, toluene, tetrahydrofurane, methanol, dichloromethane) indicating the network formation.



**Figure 8.** Photo of the gel obtained by linking  $P((EO)_2MA)-b-PIB-b-P((EO)_2MA)$  block copolymers via ATRP of EGDMA after purification.

The product was purified via extraction with tetrahydrofuran, dichloromethane, acetone and methanol. The gel fraction was 65% after these extraction steps. The formed gel swells in polar solvents (water) and also in apolar solvents (hexane). The swelling ratio was 10% in water and 50% in hexane which indicates the amphiphilic characteristic of the gel. In toluene, which is good solvent for both the hydrophobic and for the hydrophilic segments, the swelling ratio was 460%.

The gel and the block copolymer was also investigated by differential scanning calorimetry (DSC) (Figure 9). For the block copolymer, glass transitions of both segments appear (two inflection points can be seen on the curve at temperature regions where the DSC curves of pure polyisobutylene and poly(poly(ethylene oxide) methacrylate) show also inflection points) although the glass temperature of the di(ethylene oxide) methacrylate (-38 °C) is lower by 10 °C than that for the homopolymer (-28 °C). For the conetwork, only the glass transition of polyisobutylene can be observed at -62 °C.



**Figure 9.** Differential scanning calorimetric curves.

Amphiphilic triblock copolymers were also synthesized by ATRP using different hydrophilic monomers, namely di(ethylene oxide) methyl-ether-methacrylate, poly(ethylene oxide) methyl ether methacrylate ( $M = 300$  g/mol), di(ethylene oxide) ethyl ether acrylate and poly(ethylene oxide) methyl ether acrylate ( $M = 480$  g/mol), and 2-bromoisobutyrate-telechelic polyisobutylene macroinitiator (**5**) with  $M_n = 11200$  g/mol. After the reactions for 71 h reaction time, samples were withdrawn and ethyleneglycol dimethacrylate was added to the reaction mixtures under the same conditions. The conversions



were determined by  $^1\text{H}$ -NMR spectra of the samples in the same way described above (Table 1). However, the characteristic methylene peak of the polymerized monomeric units has different chemical shift values in the case of the acrylates (4.20 ppm for di(ethylene oxide) ethyl ether acrylate and 4.16 ppm for poly(ethylene oxide) methyl ether acrylate) than in the case of methacrylates (4.10 ppm).

**Table 1.** The conversions reached in the ATRP-polymerizations of different hydrophilic monomers after 71 h reaction time.

monomer	conversion
di(ethylene oxide) ethyl ether acrylate	90
poly(ethylene oxide) methyl ether acrylate	60
di(ethylene oxide) ethyl ether methacrylate	100
poly(ethylene oxide) methyl ether methacrylate	100

The conversion values show that the polymerization of methacrylates can be performed with higher efficiency. Since the characteristic peak of the non-reacting 2-bromoisobutyrate chain ends at 4.14 ppm is not visible in the  $^1\text{H}$  NMR spectra, we can state that the initiator efficiency was near to 100% in each case.

**Table 2.** Gel fractions and swelling ratios in water and hexane of conetworks formed by linking block copolymers with different hydrophilic monomer units.

hydrophilic monomer		gel fraction, (%)	swelling ratio	
name	molar mass, (Da)		in water, (%)	in hexane, (%)
di(ethylene oxide) ethyl ether acrylate	188	36	7	47
poly(ethylene oxide) methyl ether acrylate	480	22	49	14
di(ethylene oxide) methyl ether methacrylate	188	61	8	43
poly(ethylene oxide) methyl ether methacrylate	300	43	20	20

Since the obtained conetworks swelled in both water and hexane, we can state that amphiphilic conetworks were formed in our experiments. The data in Table 2 also show that as expected, the longer poly(ethylene oxide) side chains result in higher swelling ratio in water and lower swelling ratio in hexane.

## CONCLUSIONS

In the course of our work bifunctional 2-bromoisobutyrate-telechelic polyisobutylene macroinitiators were synthesized via quasiliving carbocationic polymerization of isobutylene and subsequent chain end modification. Quasiliving atom transfer radical polymerization of different poly(ethylene oxide) (meth)acrylates was also performed using the polyisobutylene macroinitiator and novel amphiphilic triblock copolymers (P(PEOMA)-*b*-PIB-*b*-P(PEOMA)) were synthesized.

Bifunctional monomer ethyleneglycol dimethacrylate was also polymerized using the block copolymers as macroinitiator, and novel amphiphilic conetworks, which swell in both water and hexane, were obtained in this way.

## EXPERIMENTAL SECTION

### *Synthesis of 2-bromoisobutyrate-telechelic polyisobutylene macroinitiator (5)*

Synthesis of 2-bromoisobutyrate-telechelic polyisobutylene macroinitiator (**5**) was performed using methods described in the literature [9, 13]. Quasiliving carbocationic polymerization of isobutylene was performed in dichloromethane:hexane (45:55 V/V) solvent mixture under nitrogen atmosphere at -78 °C. Bifunctional 5-*tert*-butyl-1,3-dicumyl-chloride (**1**) was used as initiator (0,005 M), TiCl<sub>4</sub> as coinitiator (0,06 M) and tetramethyl-ethylenediamine as nucleophilic additive (0,01 M). The chains (**2**) were terminated at the end of the polymerization with allyl-trimethylsilane (it was in twofold amount relative to the chain ends). The obtained allyl-telechelic polyisobutylene (**3**) was dissolved in tetrahydrofuran and reacted with 9-borabicyclononane (9-BBN) solution (in fivefold amount of 9-BBN relative to the chain ends). Subsequently, alkaline H<sub>2</sub>O<sub>2</sub> solution was added to the reaction mixture at 0 °C to get hydroxyl-telechelic polyisobutylene (**4**). In the last step, hydroxyl-telechelic polyisobutylene was reacted with 2-bromoisobutyryl-bromide in the presence of 4-dimethylaminopyridine (both of them was added in fivefold amount relative to the chain ends) resulting in 2-bromoisobutyrate polyisobutylene macroinitiator (**5**). We synthesized this macroinitiator with 7500 g/mol and with 11200 g/mol number average molecular weights.

### *Synthesis of the block copolymer*

Poly(poly(ethylene oxide) methacrylate)-*b*-polyisobutylene-*b*-poly(poly(ethylene oxide) methacrylate) block copolymers were synthesized by quasiliving atom transfer radical polymerization (ATRP). 2-Bromoisobutyrate-telechelic polyisobutylene (**5**) was used as initiator, purified CuCl (in the same amount as the initiating chain ends) as catalyst and hexamethyl-triethylene-tetramine (also in the same amount as the initiating chain ends) as complexing agent. The polymerization was performed in toluene at 40 °C under oxygen-

free conditions. Ascorbic acid was also added to the reaction system to reactivate the oxidized Cu-species. Poly(ethylene oxide) (meth)acrylates with different side chain lengths (di(ethylene oxide) methyl ether methacrylate, poly(ethylene oxide) methyl ether methacrylate  $M = 300$  g/mol, di(ethylene oxide) ethyl ether acrylate and poly(ethylene oxide) methyl ether acrylate  $M = 480$  g/mol), purified by a column filled with neutral  $\text{Al}_2\text{O}_3$ , were used as hydrophilic monomers. The reaction times were 71-94 h. The obtained polymers were purified by column chromatography with neutral  $\text{Al}_2\text{O}_3$ .

#### *Synthesis of amphiphilic conetworks*

Amphiphilic conetworks were synthesized also by ATRP. In these cases, the block copolymers were used as macroinitiators and bifunctional ethyleneglycol dimethacrylate (EGDMA, 4 EGDMA molecules per chain end) as monomer. The reaction times were 40-70 h. Other conditions were the same as for the synthesis of block copolymers. The conetworks were purified by extraction with tetrahydrofuran, dichloromethane, acetone and methanol.

#### *Characterizations*

The number average molecular weight, molecular weight distribution and polydispersity of the polyisobutylene macroinitiators were determined by gel permeation chromatography (GPC) using RI- and viscosity detectors. The eluent was tetrahydrofuran. The chromatograms of the block copolymers were also recorded, however, due to the different chemical behaviour of the hydrophobic and hydrophilic segments, quantitative evaluations could not be performed.

The structure of the macroinitiators and the block copolymers was investigated by  $^1\text{H}$  NMR spectroscopy (200 MHz) at room temperature.  $\text{CDCl}_3$  with 0,03% TMS was used as deuterated solvent.

In the case of the conetworks, the gel fractions were calculated as the ratio of the mass of the piece of gels after extraction to the original mass of the same piece of gels before swelling the conetworks in tetrahydrofuran, dichloromethane, acetone and methanol. The swelling ratios were calculated as the ratio of the mass of solvent taken up by the gel to the mass of the dry gel in water and hexane.

Differential scanning calorimetry (DSC) was carried out in  $\text{N}_2$ -stream between -120 and 160 °C with 10 °C/min heating rate. The second „heat up” curves were evaluated.

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