

# AMPHIPHILIC BLOCK AND “BLOCK-LIKE” COPOLYMERS BASED ON POLY(ISOBORNYL ACRYLATE) AND POLY(ACRYLIC ACID) VIA ATRP

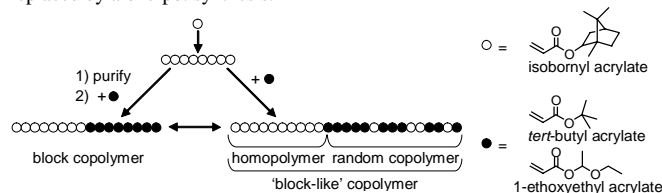
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## Introduction

Because of their pH-responsive nature and their interaction with metal ions, poly(acrylic acid) containing polymers are of vast interest for an extensive range of applications. Their application fields include cosmetics, coatings, bio-applications, drug delivery systems, and many others. Stimuli-sensitive amphiphilic block copolymers are a well-known class of intelligent polymers with a variety of promising potential applications, e.g. entrapment of environmental pollutants, catalysis, stabilizers in emulsion polymerization, drug carriers and polymeric surfactants.

In this research contribution, well-defined amphiphilic block and “block-like” copolymer structures of acrylic acid (AA) and hydrophobic isobornyl acrylate (iBA) were synthesized by atom transfer radical polymerization (ATRP) (Figure 1). The block copolymers are synthesized via the macroinitiator strategy whereas the “block-like” copolymers are synthesized via a sequential monomer addition. The major advantage of the latter synthetic approach is that time-consuming purification reactions are avoided and replaced by a one-pot synthesis.



**Figure 1:** schematic depiction of the macroinitiator strategy yielding block copolymers and sequential monomer addition yielding “block-like” copolymers.

As the ATRP mechanism is not able to polymerize AA in a direct way<sup>1</sup>, a precursor strategy was used. In this study, the use of *tert*-butyl acrylate (tBuA) and 1-ethoxyethyl acrylate (EEA)<sup>2</sup> was evaluated for the synthesis of well-defined PiBA-co-PAA copolymers after hydrolysis and thermolysis, respectively. PiBA was chosen as a hydrophobic part for the amphiphilic copolymers because of its glass transition temperature ( $T_g$ ) of 94 °C, comparable to the one of poly(methyl methacrylate) (PMMA) or polystyrene (PS). PiBA is particularly interesting as an alternative to these polymers since the ATRP synthesis of PMMA or PS with a high end group functionality (> 90 %) is not possible. Nevertheless, only a limited number of reports have been published about the synthesis of PiBA polymers.<sup>3,4</sup> Therefore, first, a detailed study of the homopolymerization of iBA by ATRP was performed.

## Experimental

**Materials.** Isobornyl acrylate (iBA, Aldrich, tech.) was purified by vacuum distillation (121 °C/18 mmHg). *Tert*-butyl acrylate (tBuA, Fluka, 98 +%) was purified by vacuum distillation (60 °C/60 mmHg). 1-Ethoxyethyl acrylate (EEA) was synthesized by the acid catalyzed addition reaction of acrylic acid to ethyl vinyl ether as described previously.<sup>2</sup> Cu(I)Br (Aldrich, 98 %) was purified by stirring with acetic acid, then by filtering and washing with ethanol and diethyl ether, and finally by drying in a vacuum oven at 70 °C. *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA, Acros, 99 +%) was distilled (85–86 °C/12 mmHg). Methyl-2-bromopropionate (MBP, Acros, 99 %) was used as received.

**Instrumentation.** Thermogravimetric analysis (TGA) was performed with a Mettler Toledo TGA/SDTA851e instrument under air atmosphere at a heating rate of 10 °C/min from 25 °C–800 °C. Infrared spectra were obtained with React-IR 4000 instrument from Mettler Toledo. Details of all other instrumentation can be found elsewhere.<sup>5</sup>

### Homopolymerization of iBA by ATRP (synthesis of macro-initiator)

A typical polymerization procedure is as follows (e.g. entry 3, Table 1). A mixture of 0.014 mol (3 mL) of the monomer iBA,  $2.13 \times 10^{-4}$  mol (0.044 mL)

of PMDETA and 1.5 mL of ethyl acetate was bubbled with N<sub>2</sub> for 1 h to remove oxygen. Cu(I)Br ( $2.13 \times 10^{-4}$  mol, 0.031 g) was added under N<sub>2</sub> atmosphere, and the reaction flask was placed in an oil bath at 75 °C. The polymerization was started by adding  $1.42 \times 10^{-4}$  mol (0.016 mL) of methyl-2-bromopropionate as the initiator. The reaction was terminated by cooling the reaction mixture in liquid nitrogen. The resulting polymer was dissolved in THF and the copper catalyst was removed by passing the diluted reaction mixture over a column of neutral Al<sub>2</sub>O<sub>3</sub>. After evaporating the excess solvent, the polymer was precipitated in methanol (10-fold excess).

**Synthesis of block copolymers of iBA and tBuA (PiBA-*b*-PtBuA) or EEA (PiBA-*b*-PEEA) by ATRP.** A typical procedure is as follows (entry 5, Table 2). The PiBA<sub>55</sub> macroinitiator (1.0 g; 0.087 mmol) was dissolved in the monomer EEA (2.44 mL; 0.017 mol). The mixture was degassed by bubbling with N<sub>2</sub> for 1 h. Cu(I)Br (0.036 g; 0.255 mmol) was added under nitrogen atmosphere and the reaction flask was immersed in a water bath thermostated at 50 °C. The polymerization was then started by adding ligand PMDETA (0.079 mL; 0.382 mmol). After termination in liquid nitrogen, the resulting block copolymers were dissolved in THF, and purified by passing through a column with neutral alumina.

**Synthesis of “block-like” copolymers of iBA and tBuA (PiBA-*co*-PtBuA) or EEA (PiBA-*co*-PEEA) by ATRP.** A typical procedure is as follows (entry 9, Table 2). A mixture of iBA (4 mL; 0.0187 mol), ethyl acetate (1.3 mL) and PMDETA (0.079 mL, 0.378 mmol) was bubbled with N<sub>2</sub> for 1 h. Cu(I)Br (0.054 g; 0.378 mmol) was added under nitrogen atmosphere and the reaction flask was immersed in a water bath thermostated at 75 °C. The polymerization was then started by adding MBP (0.028 mL; 0.252 mmol). After reaching a desired conversion, a degassed mixture of 7.27 mL (0.050 mol) EEA, 2.4 mL ethyl acetate, 0.158 mL (0.757 mmol) PMDETA and 0.090 g (0.063 mmol) Cu(I)Br was added to the solution. After termination in liquid nitrogen, the resulting block copolymers were dissolved in THF, and purified by passing through a column with neutral alumina.

**Hydrolysis of PtBuA containing copolymers and thermal deprotection of the PEEA containing precursor polymers.** The PtBuA containing copolymer was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and a three-fold excess of trifluoroacetic acid (TFA) with respect to the tBuA ester groups was added. The mixture was stirred at room temperature for 2 h. Next, the solvent and TFA were evaporated and the polymer was precipitated in cold hexane. The final polymer was dried under vacuum. For thermolysis of the PEEA containing polymers, a sample was spread out on a glass surface and heated in an oven at 80 °C for 24 hours.

## Results and Discussion

The first step for the preparation of a well-defined PiBA-PAA block copolymer consisted in the synthesis of well-defined PiBA macroinitiator. For all homopolymerizations, methyl-2-bromopropionate (MBP) was used as the initiator, in combination with Cu(I)Br/PMDETA as the catalyst system. The results for the homopolymerization of iBA by ATRP are given in Table 1.

**Table 1:** Summary of results for the synthesis of PiBA homopolymers by ATRP.

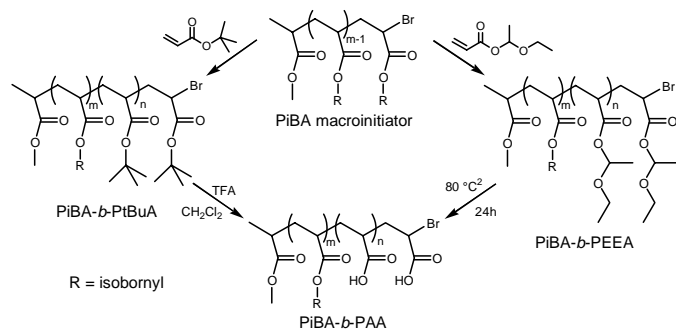
Entry	[iBA] <sub>0</sub> /[In] <sub>0</sub> /[Cu] <sub>0</sub> /[Ligand] <sub>0</sub> <sup>a</sup>	Solvent	Conv. <sup>b</sup> (%)	M <sub>n,exp</sub> <sup>c</sup> (g·mol <sup>-1</sup> )	M <sub>w</sub> /M <sub>n</sub>
1 <sup>d</sup>	75/1/1/1	Acetone	7	2100	1.19
2 <sup>e</sup>	100/1/0.5/0.75	EtOAc	23	3300	1.26
3 <sup>e</sup>	100/1/1.5/1.5	EtOAc	93	14500	1.16

<sup>a</sup> = initial concentration monomer, initiator, copper catalyst and ligand, respectively, <sup>b</sup> calculated from <sup>1</sup>H-NMR, <sup>c</sup> relative to polystyrene standards, <sup>d</sup> polymerization temperature is 50 °C, <sup>e</sup> polymerization temperature is 75 °C.

With acetone as a solvent (entry 1), the polymerization rate was quite low, as a result of the applied polymerization temperature (boiling point). Reasonable polymerization rates could only be obtained by using an excess of Cu(I)Br (4 eq. relative to initiator). When ethyl acetate was used as a solvent, higher polymerization rates could be obtained with a lower Cu concentration (entry 2). Conversions up to 90% with a polydispersity index (PDI) of 1.16 could be obtained when the Cu concentration was increased from 0.5 to 1.5

equivalents (entry 3). The controlled character for all polymerization reactions was proved by the linear increase of the number average molecular weight as a function of conversion, while the PDI remains narrow. Also the first order kinetic plot shows a linear behaviour. Furthermore, MALDI-TOF MS analysis confirmed the controlled character of the polymerization.

The above synthesized PiBA homopolymers were used as a macroinitiator for the synthesis of amphiphilic PiBA-*b*-PAA block copolymers. Both tBuA and EEA were evaluated as precursor monomers for the preparation of the PAA segment (Figure 2).



**Figure 2:** Synthetic strategy for the synthesis of PiBA-*b*-PAA block copolymers.

**Table 2** (entry 4-6) gives an overview of the performed block copolymerizations. In all cases, three equivalents of Cu catalyst to the macroinitiator concentration were used in order to have a sufficiently fast polymerization rate. By varying the macroinitiator and using different reaction conditions, a variety of PiBA-*b*-PAA block copolymers was prepared with different ratio of PiBA/PAA and lengths of both segments. In all cases, well-defined block copolymers with a controlled molecular weight and a narrow molar mass distribution were obtained. Also, in GPC analysis, no unreacted macroinitiator could be observed.

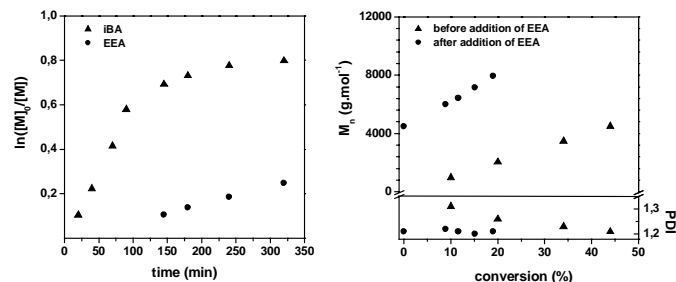
**Table 2:** Summary of results for the synthesis of PiBA-PtBuA and PiBA-PEEA block and “block-like” copolymers by ATRP.

Entry	$M_{n,exp}^a$ (g.mol <sup>-1</sup> )	$M_w/M_n$	Composition <sup>b</sup>
4	16600	1.23	PiBA <sub>73</sub> - <i>b</i> -PtBuA <sub>98</sub>
5	13700	1.21	PiBA <sub>55</sub> - <i>b</i> -PEEA <sub>38</sub>
6	14100	1.22	PiBA <sub>17</sub> - <i>b</i> -PEEA <sub>72</sub>
7	26600	1.25	iBA <sub>54</sub> /iBA <sub>9</sub> /tBuA <sub>126</sub> <sup>c</sup>
8	9000	1.17	iBA <sub>46</sub> /iBA <sub>2</sub> /EEA <sub>13</sub> <sup>c</sup>
9	9800	1.22	iBA <sub>34</sub> /iBA <sub>9</sub> /EEA <sub>46</sub> <sup>c</sup>

<sup>a</sup> relative to polystyrene standards, <sup>b</sup> calculated by <sup>1</sup>H-NMR, <sup>c</sup> notation “block-like” copolymers: before double line PiBA segment with average DP and after double line, composition second segment after addition of second monomer.

In addition to the synthesis of block copolymers via the macroinitiator strategy, copolymers of iBA and AA were also prepared via a sequential monomer addition, leading to the formation of “block-like” copolymers (Figure 1). The molecular architecture of this type of copolymers is intermediate between those of block and random copolymers. Therefore, the repulsive inter-chain interactions are less strongly changing along the chain in comparison with a conventional block copolymer. Because of this, these polymers may be of particular interest for specific applications such as stabilization of dispersions. **Table 2** (entry 7-9) gives an overview of the performed reactions. In all cases, copolymers with a controlled molecular weight and low polydispersity index were obtained. The increase of the molecular weight as a function of time shows a linear behavior, even after the addition of the second monomer, while the PDI remains low during the polymerization reaction (Figure 3, right). The first order kinetic plot of the polymerization of both monomers also shows a linear behavior (Figure 3, left). After addition of the EEA monomer, the polymerization rate of iBA decreases as a result of the dilution of the reaction mixture. GPC analysis

revealed that the initiator efficiency of the first PiBA segment is high, but not quantitative: a small tailing is visible in the chromatogram. Based on the reactivity ratios of both monomers (iBA and tBuA or EEA), it was concluded that the resulting polymers consist of a first block of pure iBA and a reversed gradient block of iBA and tBuA or EEA.



**Figure 3:** Synthesis of “block-like” copolymers of iBA with EEA [entry 9, Table 2] (left) first order kinetic plot, (right) increase of  $M_n$  and evolution of PDI (before and after addition of EEA) as a function of conversion (after addition of EEA, the total conversion of iBA and EEA, since the addition, is used).

In a next step, the PiBA-PtBuA copolymers were hydrolysed to PiBA-PAA by means of TFA. FTIR analysis revealed the hydrolysis of the *tert*-butyl ester group to a carboxylic acid. However it was also found that the isobornyl ester is not stable under these reaction conditions. This shows that the *tert*-butyl protecting group strategy is not suitable to synthesize amphiphilic PiBA-PAA copolymers. Therefore the 1-ethoxyethyl protecting group strategy was considered. In this case, deprotection is done by simple heating. TGA analysis showed complete and selective deprotection of the PEEA segment without danger for degradation of the PiBA segment. <sup>1</sup>H-NMR analysis also confirmed total conversion of PiBA-PEEA copolymers to PiBA-PAA copolymers, as the characteristic signals of PEEA have completely disappeared and a signal arising from the carboxylic acid functionalities is observed.

Currently, we are investigating the pigment stabilization abilities of the “block-like” copolymers in comparison to block copolymers prepared via the macroinitiator strategy.

## Conclusion

We have reported on the synthesis of amphiphilic PiBA containing copolymers by ATRP. First a detailed kinetic study was performed on the homopolymerization of iBA. Next, starting from well-defined PiBA macroinitiators, PiBA-*b*-PAA block copolymers with various compositions were synthesized. In addition, “block-like” copolymers of iBA and AA were prepared in a controlled way by sequential monomer addition. The tBuA as well as the EEA precursor strategy were used to synthesize precursor polymers for these copolymers. tBuA was not appropriate for the synthesis of the PAA segments as selective deprotection was not possible. On the other hand, thermal deprotection of the PEEA segments resulted in the desired amphiphilic PiBA-PAA copolymers.

## Acknowledgement

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