

PP/PMMA Block Copolymers by Combination of ATRP and Metallocene Catalysis

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Summary: PP-*b*-PMMA has been synthesized by a combination of metallocene catalysis and the controlled radical polymerization technique ATRP. $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ and $(\text{Me}_4\text{Cp})\text{-SiMe}_2(\text{N-tert-Bu})\text{TiCl}_2/\text{MAO}$ were used for the synthesis of atactic polypropylene. By a series of chemical modifications pp macroinitiators for the ATRP polymerization of MMA were synthesized. The PP-*b*-PMMA with polydispersities from 1.8–2.8 and an M_n ranging from 8 to 26 kg/mol was characterized by $^1\text{H-NMR}$, SEC and DSC.

Keywords: ATRP; block copolymers; metallocene catalysis; poly(methyl methacrylate); poly(propylene)

Introduction

Isotactic polypropylene is a widespread commodity plastic due to its favourable combination of low production costs and excellent product properties. However a major drawback is the low adhesion to polar materials such as glass, paintings or to other non-olefinic polymers like poly(acrylates), poly(methyl methacrylates) or poly(amides). This can be improved by the use of block copolymers which act as compatibilizers for instance diblock copolymers or graft copolymers. Most of the compatibilizer used to improve the interaction to polar substrates are graft copolymers which can be produced easily on a large scale by reactive extrusion. However no diblock copolymers are known to be in use for this application. This is caused by the limited possibilities for the synthesis of block copolymers from propylene and non-olefinic monomers. The reported block copolymers were obtained by quasi living systems such as $\text{V}(\text{acac})_3/\text{AlEt}_2\text{Cl}$ at -65°C [1,2] or $\text{Cp}_2\text{ZrMe}_2/\text{B}(\text{C}_6\text{F}_5)_3$ [3]. But these reactions have to be carried out under

extreme purity and with a high synthetically effort. This work presents a synthetic pathway for PP/PMMA block copolymers by a combination of metallocene catalysis and controlled radical polymerization techniques.

In the first step propylene was polymerized by the metallocene catalyst systems $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ (Cat 1) and $(\text{Me}_4\text{Cp})\text{SiMe}_2(\text{N-tert-Bu})\text{TiCl}_2/\text{MAO}$ (CBT/Cat 2) which can be seen in Figure 1. During metallocene catalysis polypropylene chains terminate predominately by α -hydride elimination. The resulting double bond can be transformed by chemical reactions to an initiating point for the atom transfer radical polymerization (ATRP).

The resulting macro initiator can be used for the polymerization of monomers suitable for radical polymerization with good control over molar mass, block length and polydispersity.

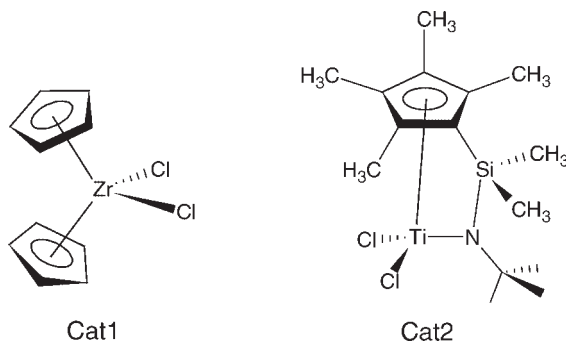
Results and Discussion

Polymerization of Propylene

The results and the conditions of the polymerizations can be found in Table 1.

Atactic polypropylenes with a M_n ranging from ~ 3600 to ~ 4900 g/mol for catalyst 1 and ~ 6500 to ~ 15400 g/mol for catalyst 2 were obtained. The concentration of vinylidene

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**Figure 1.**

Catalysts used for polymerization of propylene.

groups at the end of the polymer chain was determined by $^1\text{H-NMR}$ spectroscopy. As expected for both catalyst systems only the signals for the vinylidene groups (Figure 2) could be found since both catalyst systems are known to terminate predominately by β -hydride elimination.

It has been shown by other groups that vinyl or vinylidene terminated polypropylene can be modified by a broad variety of chemical reactions (Figure 3).

In order to synthesize a macro initiator for ATRP the aim of the modification was to introduce a C-Br functionality to each polypropylene chain. We tried three general pathways for the modification:

- a) Epoxidation of the double bond followed by ring opening reactions and esterification with 2-bromoisobutyryl bromide (Figure 4).

Table 1.

Polymerization of propylene with catalyst 1 and 2.

Sample	P _{propylene}	[CAT]	M _n ^{a3)}
	[bar]	[mol/l]	[g/mol] (PD)
PP2c ¹⁾	2	$2.6 \cdot 10^{-5}$	3900 (1.35)
PP2d ¹⁾	4	$1.3 \cdot 10^{-5}$	4900 (1.50)
PP2g ¹⁾	2	$2.6 \cdot 10^{-5}$	3600 (1.3)
PP2i ¹⁾	3	$5.2 \cdot 10^{-5}$	3800 (1.33)
A2 ²⁾	2	$2.6 \cdot 10^{-5}$	15400 (1.79)
A4 ²⁾	2	$2.6 \cdot 10^{-5}$	9000 (1.70)
PP5 ²⁾	2	$2.6 \cdot 10^{-5}$	14100 (1.75)
PP6 ²⁾	2	$2.6 \cdot 10^{-5}$	8200 (1.81)
PP7 ²⁾	2	$2.6 \cdot 10^{-5}$	5900 (1.73)

¹⁾ catalyst 1/MAO Al/Ti = 1000/1, toluene.

²⁾ catalyst 2/MAO Al/Zr = 1000/1, toluene.

³⁾ obtained by SEC – universal calibration.

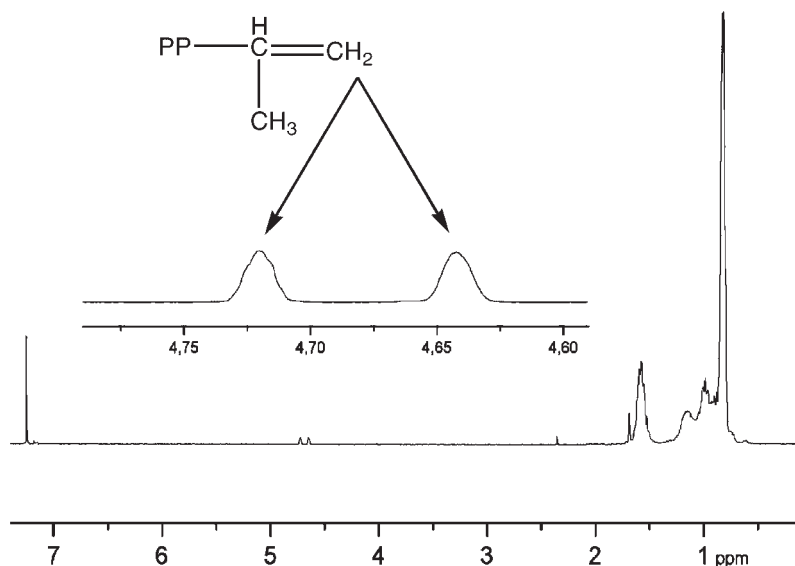
- b) Bromating of the double bond (Figure 5).
- c) Hydroboration followed by an esterification with 2-bromoisobutyryl bromide (Figure 6).^[7,8]

a) Epoxidation of the Double Bond Followed by Ring Opening Reactions and Esterification with 2-Bromoisobutyryl Bromide (Figure 4)

The epoxidation of polyolefins containing double bonds has been investigated by our group in the past^[9]. M-Chloroperbenzoic acid (MCPBA) proved to be the most convenient agent, since the reaction can be carried out at room temperature and reaches 100% conversion after 24 hours. After the epoxidation the transformation to an ATRP initiator molecule can be achieved by ring opening under anhydrous conditions with a base and *in situ* addition of 2-bromoisobutyryl bromide (A2–A4). Ring-opening can also be achieved under acidic conditions with hydrochloric acid (A1). In this case after esterification a polypropylene carrying two ATRP initiating sites is obtained. The completeness of the reactions was confirmed by $^1\text{H-NMR}$ spectroscopy.

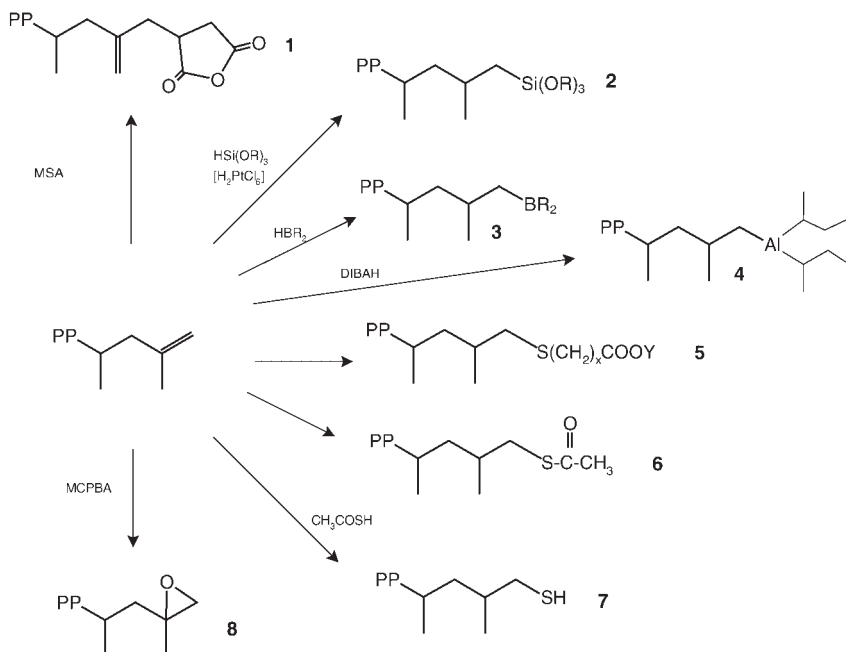
b) Bromating of the Double Bond (Figure 5)

Also the bromination of the double bond terminated polymers was investigated. It was done either directly carrying out the reaction with HBr or Br₂ or indirect by a reaction with DiBAH followed by the

**Figure 2.**¹H-NMR spectroscopy of PP2C.

addition of Br₂. While the reaction B1 and B2 would result in a polypropylene with one ATRP initiating group per chain reaction B3 would lead to two initiating

sites per chain. Assuming both initiating sites start the polymerization of MMA effectively a three armed star with two PMMA arms would be obtained. The

**Figure 3.**

Chemical modification of vinylidene terminated polypropylene [4–6].

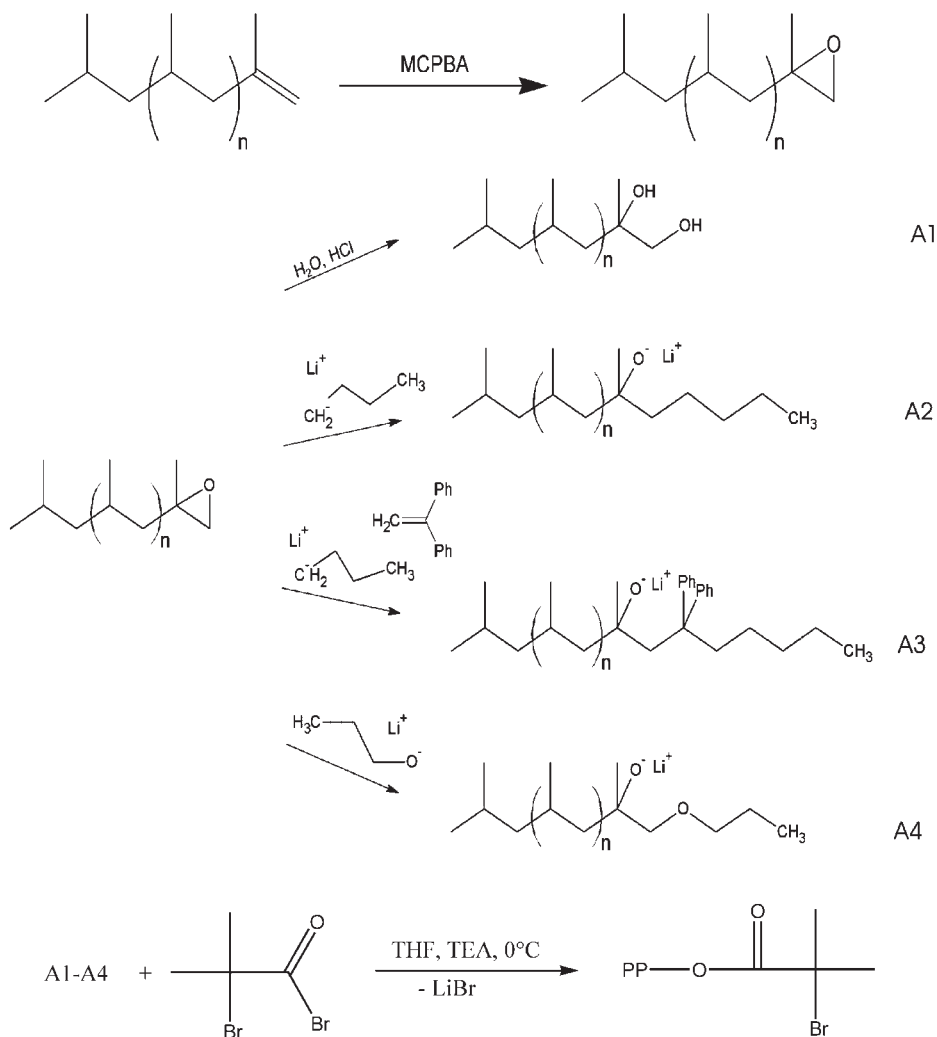


Figure 4.

obtained macro initiators were characterized by ^1H -NMR spectroscopy.

c) Hydroboration Followed by an Esterification with 2-Bromoisobutyryl Bromide (Figure 6)^[7,8]

As can be seen in reaction path c) (Figure 6) a transformation of the double bond to a mono hydroxyl functionality can be achieved by a hydroboration with 9-BBN followed by an oxidation of the borane group with hydrogen peroxide under basic conditions. After esterification with 2-bromoisobutyryl bromide a polypropylene

carrying one ATRP initiating site per molecule can be obtained. Completeness of reactions was confirmed by ^1H -NMR spectroscopy.

Synthesis of PP/PMMA Block Copolymers by ATRP

ATRP macro initiators which were obtained by the three reaction pathways were investigated towards their ability to initiate the polymerization of MMA under ATRP conditions. All of them were able to initiate a MMA polymerization. The results concerning the obtained polydispersity and

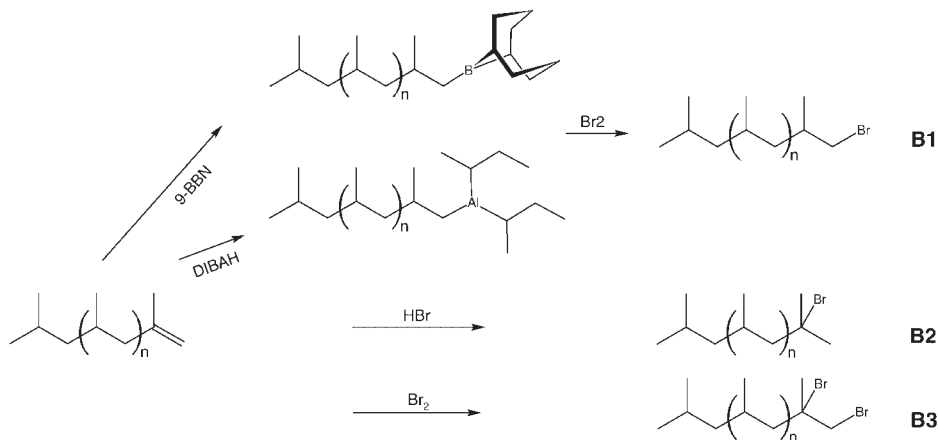


Figure 5.

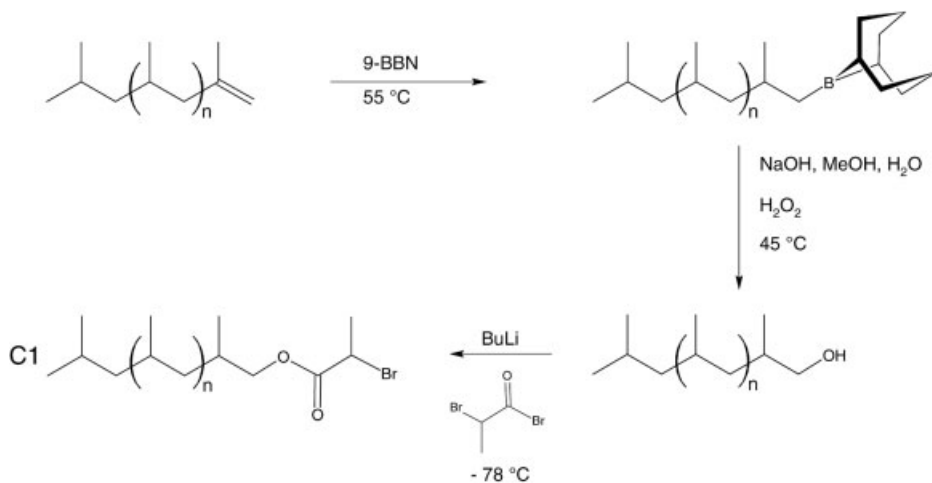


Figure 6.

completeness of initiation differed however.

If the macro initiator was synthesized by direct or indirect bromination the obtained block copolymers showed SEC chromatograms with clearly bimodal shape (Figure 7). This has been expected since for an inactivated C-Br bond (no carbonyl or aromatic group nearby) the rate constant for activation k_{act} and deactivation k_{deact} are smaller than for the propagation k_{prop} . For a controlled radical polymerisation k_{act} and k_{deact} have to be bigger than k_{prop} and the equilibrium between activated and dormant species has to be clearly on side of dormant species.

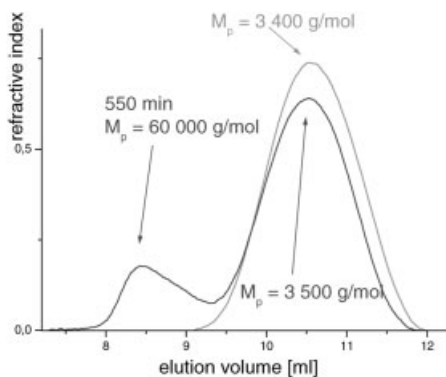
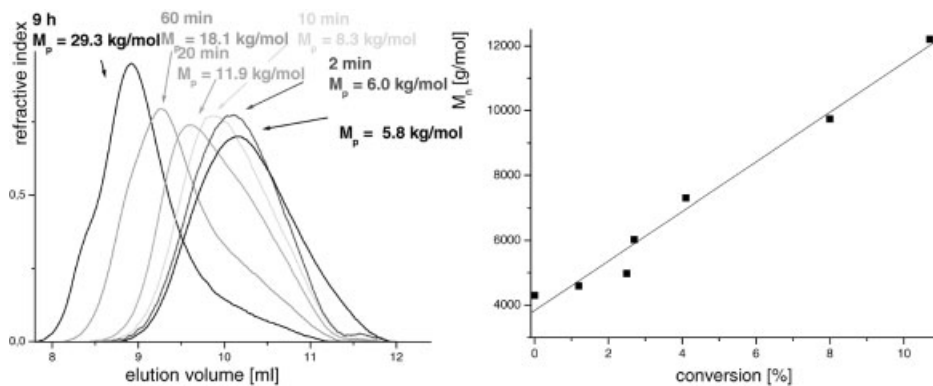


Figure 7.

SEC chromatogram for a PP-b-PMMA obtained from a macro initiator obtained by B1.

**Figure 8.**

Left – increase of molar mass starting from a macro initiator C1 Right – increase of molar mass in dependency of conversion.

For all the macro initiators carrying bromoisobutyryl groups, obtained by reaction pathway a) and c) a complete initiation of MMA polymerization was observed, leading to PP/PMMA block copolymers with a monomodal SEC chromatogram (Figure 8). The best results were achieved for the macro initiators obtained by reaction pathway c) while for macro initiators obtained with reaction pathway a) somewhat broader polydispersities were obtained. This could be caused by an incomplete modification of all double bonds undetected due to the limits of analysis by $^1\text{H-NMR}$ spectroscopy.

As can be seen in Figure 8 the increase of M_n is linear to the conversion which is typical for the controlled radical polymerization. In the following only the results of the synthesis of PP/PMMA block copoly-

mers deriving from macro initiators C1 are presented in Table 2.

Characterization

The synthesized PP/PMMA block copolymers were characterized by DSC for their thermal properties (Table 3). Since the chosen catalyst system gives atactic polypropylene no melting peak was detected. As can be seen in Figure 9 two separated glass transition temperatures can be found. The lower one corresponds to atactic polypropylene but is unusual low due to the low M_n . The higher glass transition temperature corresponds well with values measured by us for PMMA made by ATRP. Since the values of the glass transition temperatures are well within the range of the values found for the homopolymers a good phase separation can

Table 2.

Results and conditions of MMA polymerization by ATRP.

run	T_p	[Initiator]/[CuBr]/ [PMDETA] ²⁾			$M_n(D)^1$ (PP)	$M_n(D)^1$ (PP-block-PMMA)	ratio PP/PMMA
	[°C]	[mmol/l]			[g/mol]	[g/mol]	
2	80	37.9	37.5	37.5	4900 (1.52)	7 900 (2.02)	1:0.6
1	25	71.0	39.5	32.7	4900 (1.52)	14 000 (2.05)	1:1.9
4	25	36.3	19.4	18.6	4300 (1.27)	16 800 (1.77)	1:2.9
3	40	23.3	24.2	23.1	4400 (1.6)	19 700 (2.75)	1:3.5
7	25	22.3	24.4	23.1	4300 (1.27)	26 300 (2.11)	1:5.1

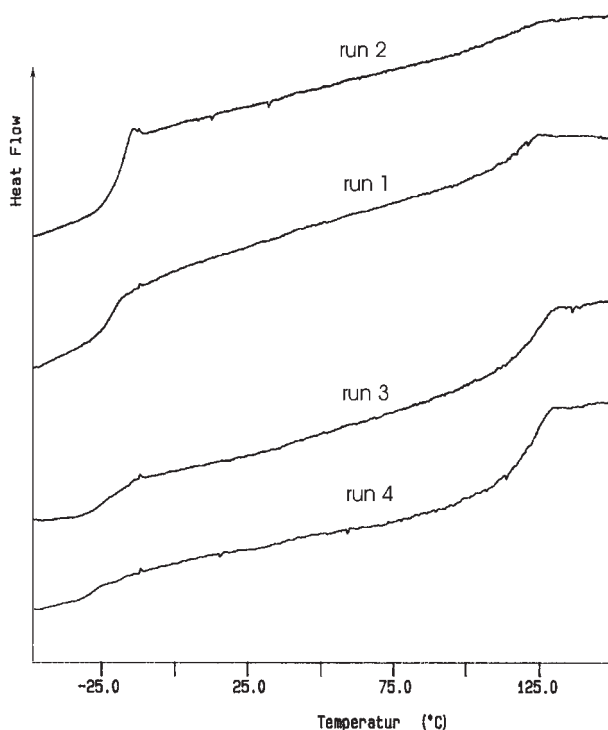
¹⁾ Obtained by SEC-universal calibration.

²⁾ [MMA] 9.4 mol/l, no additional solvent.

Table 3.

Thermal characterization of PP-b-PMMA.

run	1. T_g (ΔC_p)	2. T_g (ΔC_p)	$M_n^{1)}$ (PP)	$M_n^{1)}$ (PMMA)
	[°C] [J/g·K]	[°C] [J/g·K]	[g/mol]	[g/mol]
2	−18.2 (0.340)	119.9 (0.083)	4 900	3 000
1	−21.6 (0.142)	117.7 (0.142)	4 900	9 100
4	−28.1 (0.157)	118.9 (0.270)	4 300	12 500
3	−24.1 (0.116)	122.3 (0.179)	4 400	15 300
6	−25.3 (0.069)	120.2 (0.221)	4 300	19 800
7	−27.8 (0.048)	120.7 (0.230)	4 300	22 000

¹⁾ Obtained by SEC-universal Calibration.**Figure 9.**

DSC curves of PP/PMMA block copolymers.

be assumed. The values of the PMMA glass transition temperature seems to increase with the M_n of the PMMA block. This could be caused by a higher ratio of mixed phase for diblock copolymers with shorter PMMA blocks.

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