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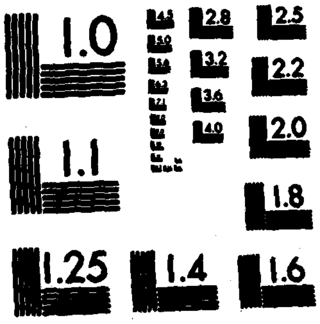

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SYNTHESIS OF CONJUGATED POLYMERS WITH ALTERNATING AROMATIC AND QUINONOID SEQUENCES VIA ELIMINATION ON PRECURSORS

by

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An elimination reaction for the formation of conjugated polymers from polymer precursors containing alternating sp^3 carbon atom and conjugated segments in the main chain is described. The resulting conjugated polymers with alternating aromatic and quinonoid sequences are inaccessible by conventional polymerization processes. The π-electron conjugation extension process is exemplified by reactions performed on poly(5,5',α-bithiophenediyl p-acetoxybenzylidene) at 23°C and followed by electronic and infrared spectra. The semiconductor band gap narrowed from an initial value of 1.53 ev for the precursor polymer to about 0.83 ev for the conjugated derivative. Further evidence for the sp^3 to sp^2 carbon atom conversion by the elimination process is provided by infrared data.

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ABSTRACT

An elimination reaction for the formation of conjugated polymers from polymer precursors containing alternating sp^3 carbon atom and conjugated segments in the main chain is described. The resulting conjugated polymers with alternating aromatic and quinonoid sequences are inaccessible by conventional polymerization processes. The π-electron conjugation extension process is exemplified by reactions performed on poly(5,5',α-bithiophenediyl p-acetoxybenzylidene) at 23°C and followed by electronic and infrared spectra. The semiconductor band gap narrowed from an initial value of 1.53 ev for the precursor polymer to about 0.83 ev for the conjugated derivative. Further evidence for the sp^3 to sp^2 carbon atom conversion by the elimination process is provided by infrared data.

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The many synthetic routes to conjugated polymers may be classified into two broad categories: (i) those in which the target conjugated polymer is obtained directly from conventional polymerization processes[1-2]; and (ii) those involving transformation of an existing precursor nonconjugated polymer into the target conjugated polymer.[2] The latter approach is especially attractive from a technological application point of view since the precursor polymers are usually soluble or fusible whereas the conjugated derivatives are usually more intractable. Elimination of small molecules from precursor polymers is an important class of transformation processes for forming conjugated polymers. Two applications of polymer elimination reactions to the synthesis of conjugated polymeric conductors have recently been reported. Edwards, Feast and their co-workers have described synthesis of polyacetylene films by thermal elimination of aromatic hydrocarbons such as 1,2-bis-(trifluoromethyl)benzene, naphthalene and anthracene from films of soluble saturated precursor polymers.[3] Lenz, Karasz and co-workers have reported the synthesis of poly(p-phenylene vinylene) (PPV) films by thermal elimination of $(CH_3)S$ and HCl from poly(p-xylene- α-dimethylsulfonium chloride), a soluble polyelectrolyte.[4]

In the synthesis of conjugated polymers via elimination reactions the initial degree of saturation could range from a minimum of one sp^3 carbon atom separating unsaturated segments in the chain to a maximum of an all-sp^3 carbon chain. Typically, two sp^3 carbon atoms separate conjugated segments in the polymer chain; a double bond is formed between these two sp^3 carbons by elimination of low molecular weight molecules. This is the case with the polyacetylene[3] and PPV[4] syntheses from precursors previously mentioned and indeed with most known double bond forming organic elimination reactions.[5-7] We have discovered that polymer chains in which one sp^3 carbon atom (-CRH-) alternates with unsaturated segments, undergo elimination reactions expelling the bridge hydrogens under oxidative or reductive conditions. The general redox elimination process is illustrated in scheme 1 of Figure 1 where D or A denotes π-electron donor or π-electron acceptor conjugated segments of a polymer main chain. In principle this redox process can be chemical or electrochemical and can be carried out with the polymer substrate in the solid state or in solution.

The redox elimination process is exemplified by reactions performed on poly(5,5', α-bithiophenediyl p-acetoxybenzylidene)(PBTAB) as shown by scheme 2, Figure 1, where X = S and R = p-acetoxyphenyl. The synthesis and characterization of PBTAB and related polymers containing sp^3 carbon (-CRH-) bridges between conjugated segments are described elsewhere.[8,9] The PBTAB samples used in experiments described here have intrinsic viscosity of 0.12 dl/g in N,N-dimethylformamide (DMF)and an estimated $DP_n \sim 1250$. In order to follow progress of elimination, reactions where performed in a sealed glass vessel using thin films of PBTAB cast from tetrahydrofuran (THF) solutions onto sapphire (UV-VIS-NIR) and KCl (IR) substrates while monitoring the electronic or infrared spectra at room temperature (23°C) in situ.[10] Initially, the optical absorption or FTIR spectrum of the PBTAB film was recorded and then bromine vapor was introduced into the reaction vessel. Subsequently, FTIR spectra in the 250-4000 cm^{-1} region were recorded every 90 seconds using a Digilab Model FTS-14 spectrometer and optical absorption spectra in the 185-3200 nm (0.39-6.70 ev) range were recorded every 15 minutes[11] using a Perkin-Elmer Model Lambda 9 UV-VIS-NIR spectrophotometer. The reactions were continued until no visible changes were detected in the spectra.

Figure 2 shows FTIR spectra of PBTAB film at different times during in situ elimination reaction at 23°C. The main changes observed in the spectra are the following. The aliphatic C-H stretching vibration bands in the 2800-3000 cm^{-1} region are significantly modified; the 2870 cm^{-1} absorption band assigned to bridge sp^3-1s C-H decreases with time and eventually disappears whereas the 2960 cm^{-1} assigned to the side group methyl does not. A new gas phase band at 2400-2800 cm^{-1} attributable to HBr gas appeared even in the first spectra after reaction was started and gradually intensified. New absorption bands appeared and intensity of existing ones increased in the 1000-1600 cm^{-1} region. There was no evidence of a new band in the 500-650 cm^{-1} that would be attributable to a C-Br due to substitution or bromination reactions. These IR spectra results clearly show that the bridge hydrogens of PBTAB are eliminated as HBr by reaction with Br_2 and are consistent with the indicated conjugated derivative of PBTAB, polymer structure IIb, Figure 1. However, partial ionization of IIb is not ruled out by the IR data.

The optical absorption spectra at different times of reaction are shown on Figure 3. Saturated PBTAB (curve 1, Figure 3) is a blue polymer and has a band gap (E_g) of 1.53 ev (810 nm) and λmax = 692 nm (1.79 ev); a second peak is located at 580 nm (2.14 ev). After 15 min. reaction time[11], the electronic spectra is red shifted with E_g now located at 1.13 ev (1100 nm). Progress in elimination further narrows the band gap as curves 3 to 12 show. No observable changes in the absorption spectra were seen after 24 hours (curve 12). Visually, the sample changes from blue to metallic grey in color. E_g determined from curve 12 is about 0.83 ev ($\sim$1500 nm). This indicates about 46% reduction in the band gap of PBTAB and represents a large increase in π-electron delocalization in transforming <u>IIa</u> to <u>IIb</u> (Figure 1) by elimination.

Similar general observations on the elimination process have been made on PBTAB when reacted with iodine vapor at 50°C or I_2 and Br_2 solutions at 23°C as well as on other polymers within the class shown as <u>Ia</u> (Figure 1), for example: D = 2,5-thiophenediyl,[9] 2,5-pyrrolediyl[9] and 3,6-carbazolyl.[12] Preliminary electrochemical studies including cyclic voltammetry also indicate that irreversible redox elimination can be performed electrochemically. As anticipated, the conjugated derivatives are generally insoluble in contrast to their nonconjugated precursors.

The following points emerge from this communication. (i) A novel polymer elimination reaction has been demonstrated as a route to conjugated polymers exhibiting a large degree of π-electron delocalization or narrow band gaps[13]. (ii) The resultant conjugated polymers with alternating aromatic and quinonoid sequences are not currently accessible by conventional polymerization processes. (iii) The technique is applicable to the synthesis of doped conducting polymers.[9,12] (iv) The true mechanistic nature of the elimination reaction is as yet unclear. Studies aimed at a detailed elucidation and exploration of these points and related questions are currently in progress.

ACKNOWLEDGEMENTS

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(10) *In situ* optical absorption and infrared spectroscopy monitor of elimination reactions were performed separately but the same reaction vessel and conditions were used.

(11) Strictly, spectra 1-11 were recorded continuously at a scan rate of 240 nm/min. covering from 3200-185 nm and thus each curve from 1 to 11 took an average of 15 min.; the optical absorption edge at 1100 nm for curve 2 therefore corresponds to a reaction time of 8.75 min. Spectrum 12 was recorded 24 hours after start of reaction.

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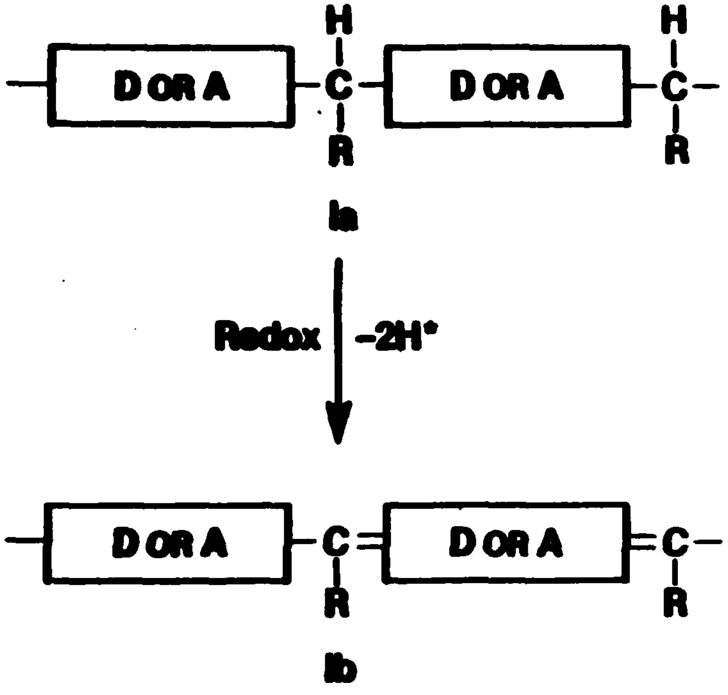
FIGURE CAPTIONS

Figure 1. Schemes of irreversible redox elimination for the formation of conjugated polymers: $H^* = H^-$ in oxidative elimination; $H^* = H^+$ in reductive elimination.

Figure 2. FTIR spectra of PBTAB film at different times during in situ elimination reaction at 23°C; G indicates a gas phase absorption band superimposed on the polymer spectra.

Figure 3. Optical absorption spectra of PBTAB film at different times during in situ elimination reaction at 23°C: 1-initial; 2-15 minutes; 12-after 24 hours.

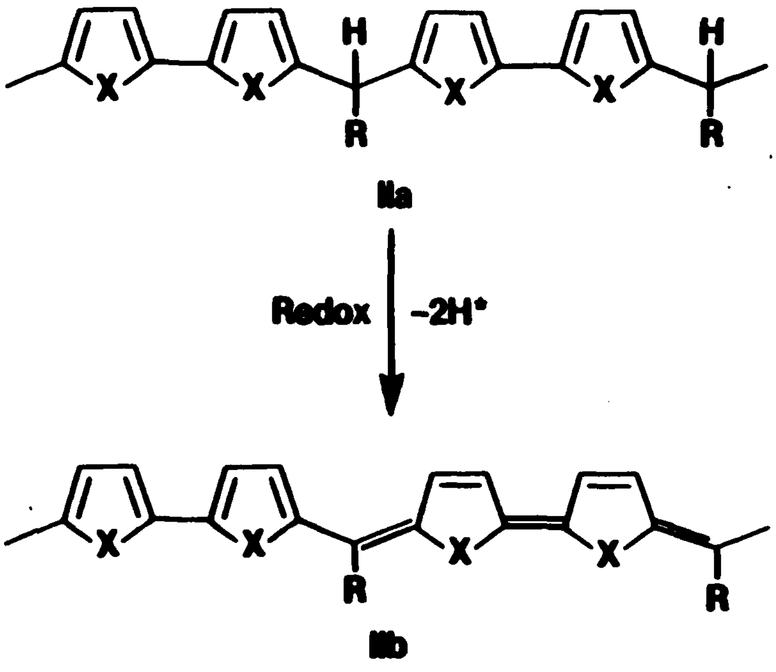
SCHEME 1



Ia

Ib

SCHEME 2



IIa

IIb

Fig. 1

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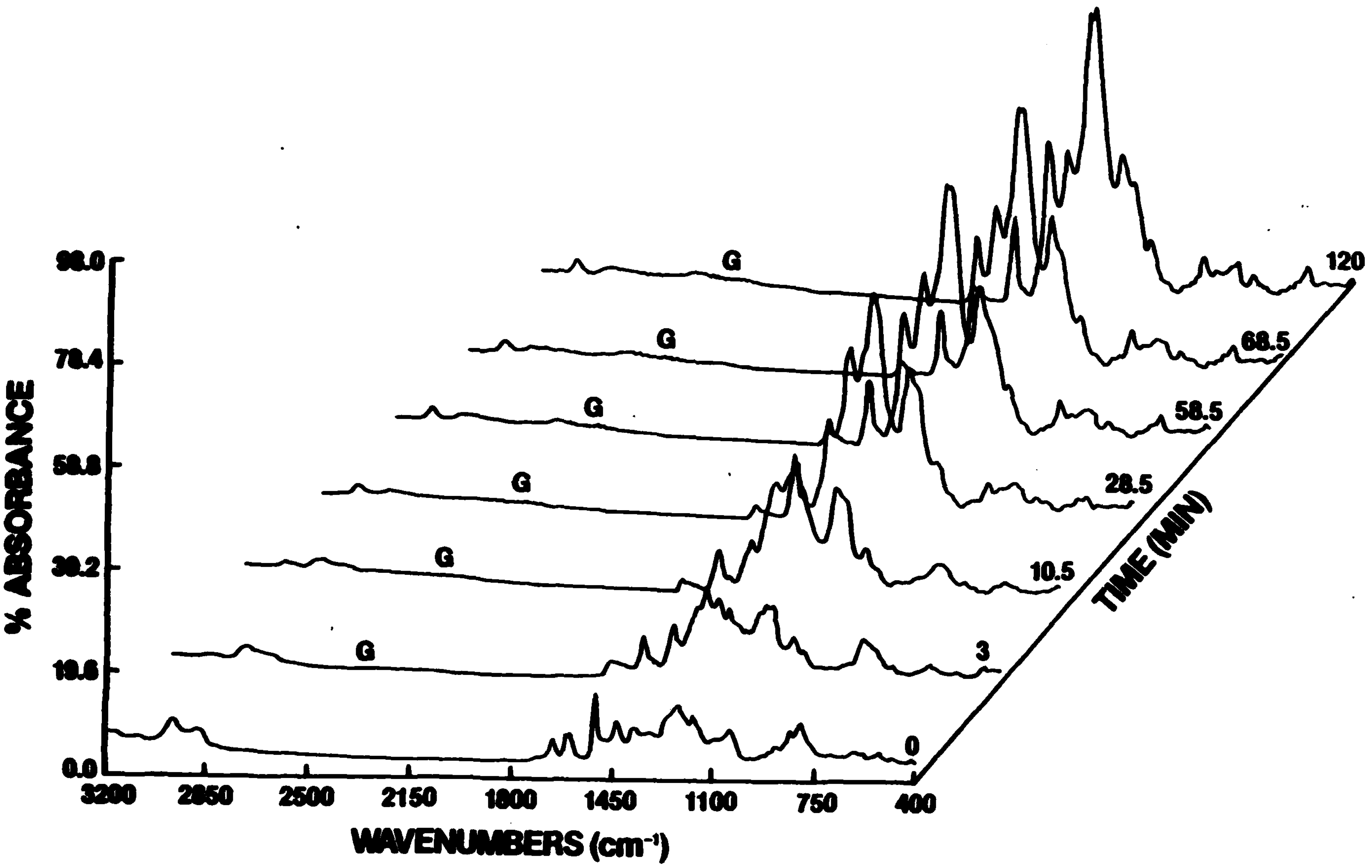
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Fig. 2

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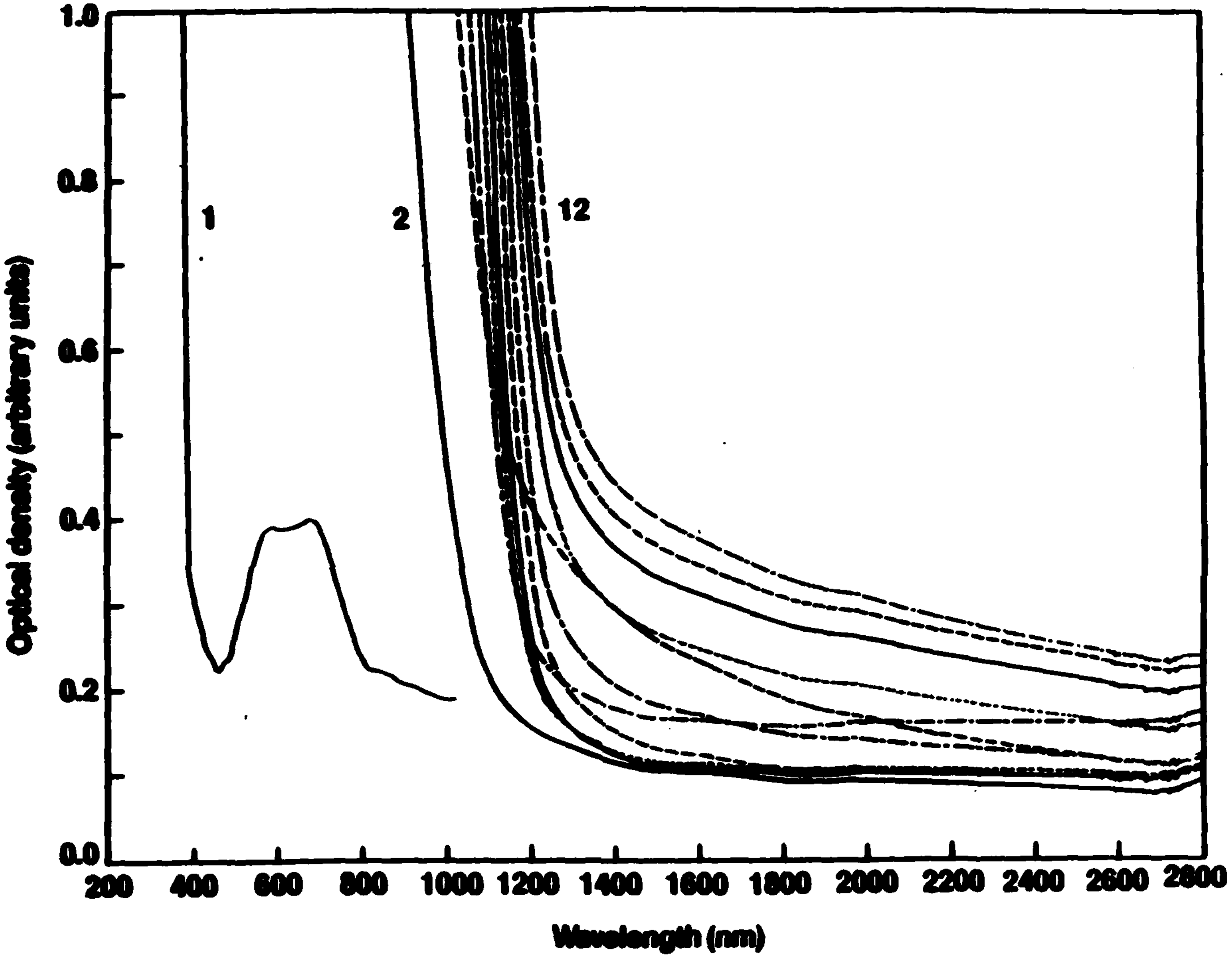
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Fig. 3

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