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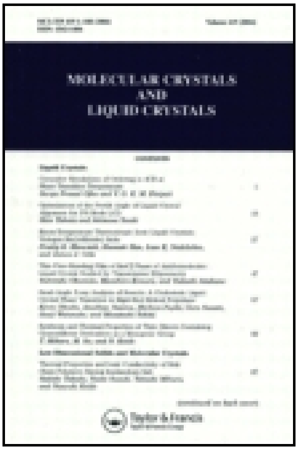

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Optimal Synthetic Design of Second-Order Nonlinear Optical Material with Good Temporal Stability

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OPTIMAL SYNTHETIC DESIGN OF SECOND-ORDER NONLINEAR OPTICAL MATERIAL WITH GOOD TEMPORAL STABILITY

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Abstract Second-order nonlinear optical copolymers containing *p*-hydroxyphenyl maleimide or 4-cinnamoyloxy-phenylmaleimide as a comonomer were newly synthesized. For improving the temporal stability, we adopted the crosslink reaction thermally and photochemically. Second-order nonlinear optical properties of the poled/cured films were investigated in terms of the second harmonic generation (SHG) and linear electro-optic (EO) coefficient measurement. SHG coefficient, d_{33} was found to be 14 pm/V at the fundamental wavelength of 1064 nm and EO coefficient, r_{33} was found to be 25-30 pm/V at 633 nm wavelength in two different crosslinked structures. To prevent the orientational relaxation of poled polymer, thermal crosslink reaction was induced using diisocyanate as a crosslinker between the side chains themselves. Another photo-crosslink was induced exposing the film at 257 nm wavelength during poling. Temporal stabilities of second-order NLO coefficients of crosslinked polymer systems were proved much better than that of guest-host system or other side chain polymers.

INTRODUCTION

Organic nonlinear optical (NLO) materials provide strong potential advantages for second harmonic generation and electro-optic applications.[1-5] Second-order NLO properties of poled polymers have been extensively studied in the past.[6] One difficulty with poled polymer was arisen from poor thermal and temporal stability of the NLO activity. The important issue for practical application with poled polymers is postulated that temporal stability of dipolar alignment should be improved. For this purpose, two methods looks quite promising; One is to synthesize the thermoplastic polymer whose glass transition temperature is very high and the other is to prepare the crosslinked polymer system.[7-8]

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In an attempt to improve both the second-order NLO effect and its temporal stability, we designed and synthesized the copolymers that has a high T_g and a high chromophore concentration in copolymer structure. In addition to the inherent backbone rigidity, the copolymer possesses carbamate group in the side chain, which would promote interactions between the polymer chains or side chain chromophores through inter- or intramolecular hydrogen bonding and therefore were expected to show a great enhancement of temporal stability of NLO activity. Also, we adopted the two different methods of crosslink reaction between the side chains themselves. Thermally induced and photo-induced crosslink reaction was employed using new copolymers. After we have synthesized novel copolymer, containing the piperazyl nitrostilbene NLO chromophore in the side-chain, the second-order NLO properties of crosslinked polymers were investigated by virtue of the second harmonic generation and linear electro-optic coefficient measurement.

EXPERIMENTAL

1-(4-Hydroxy-phenyl)-pyrrole-2,5-dione, (HPMI): A mixture of 15.0 g (106 mmol) P_2O_5 in 50 ml DMF and 8.00 g conc. H_2SO_4 was added over 15min to a solution of 30.0 g (360 mmol) maleic anhyride and 30.6 g (280 mmol) *p*-aminophenol in 80 ml DMF at 0° C. The reaction mixture was stored at 70° C for 2 hr. It was poured into 500 ml ice water. The product was dried under vacuum. Product was purified by recrystallization in isopropanol. The yield was 56.8% (30.1 g). m.p.:194-195°C.

^{1}H NMR (DMSO-d^6) δ 9.70 (s, 1H), 7.11 (d, 2H), 7.06 (d, 2H), 6.83(d, 1H).

3-Phenylacrylic acid 4-(2,5-dioxo-2,5-dihydropyrrole-1-yl)-phenyl ester; (CIHPMI): Triethylamine (21.7 g, 135 mmol) was added to a solution of 17.0 g (89.9 mmol) HPMI in 80 ml DMF. A solution of 37.5 g (225 mmol) cinnamoyl chloride in 50 ml DMF was then added dropwise at 0 ° C. The resulting mixture was stirred for 1hr at 0° C and then 2 hr at 25° C. The product was precipitated into excess ice water. The yellow precipitate was filtered and dried in vacuum. The crude product was purified by reprecipitation from THF into n-hexane. Percent yield 95.1% (27.3 g). m.p.: 222-223 ° C.

^{1}H NMR(DMSO-d$_6$): δ 7.90 (s, 1H), 7.80-7.78 (m, 2H), 7.47-7.30 (m, 4H), 7.18 (s, 5H), 6.89 (d, 1H).

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[1-[4-(N-ethylenepiperazyl)-4'-nitrostilbene]-N-[(1,1-dimethyl-*m*-isopropenyl)benzyl]]carbamate: 4-[*N*-(2-hydroxyethyl)piperazyl]-4'-nitrostilbene (2.9 g, 8.21mmole) was dissolved in dry dimethylformamide (DMF, 200ml) at 25°C under nitrogen atmosphere. Then, a trace of dibutyltin dilaurate (0.15 mole %) was added into the mixture. This was followed by dropwise addition of *m*-isopropenyl-α,α-dimethylbenzyl-isocyanate (*m*-TMI, 1.65 g, 8.21 mmole) which was diluted in DMF (10ml) over a period of 15 minutes. The mixture was heated at 70°C for 8 hours. After cooling, the resultant solution was poured into the excess amount of cold water (1 liter). Precipitated red solid was collected and dried under vacuum at 70°C for 24 hours. It was dissolved into chloroform and the solution was dried over sodium sulfate. After concentrating the final solution, it was recrystallized into ethanol. Percent yield, 70%(wt.) m.p. 120-121°C

^{1}H-NMR (DMSO-d^6): δ 8.19 (d, 2H), 7.78 (d, 2H), 7.40 (s, 1H), 7.27 (s, 1H), 7.45 (d, 2H), 6.95 (d, 2H), 4.01 (s, 2H), 3.35 (s, 4H), 2.08 (9H), 1.54 (s, 6H), 5.06, 5.36(s, 2H), 7.55 (s, 1H), 7.37 (s, 3H)

Anal. Calcd for $C_{33}H_{38}N_4O_4$ (554.69): C, 71.46; H, 6.91; N, 10.10. Found: C, 71.10; H, 6.10; N, 9.95.

Poly{1-(4-hydroxy-phenyl)-pyrrole-2,5-dione-co-[1-[4-(N-ethylenepiperazyl)-4'-nitrostilbene]-N-[(1,1-dimethyl-*m*-isopropenyl)benzyl]]carbamate} : CP-HPMI
661 mg of HPMI (3.50mmole) and 3.80 g of NLO monomer (7.00 mmole) were introduced into the vacuum ampoule. Freshly distilled dimethylformamide (38 ml) and azobisisobutyronitrile (AIBN, 17.1 mg) were added to the ampoule. The solution was degassed. The polymerization was carried out at 80°C for 24 hours. Then, the resulting solution was poured into hot methanol to precipitate the copolymer. The copolymer was purified by reprecipitation from tetrahydrofuran into ethyl ether and dried *in vacuo* at 100°C for 48 hours.

Poly{3-phenylacrylic acid 4-(2,5-dioxo-2,5-dihydropyrrole-1-yl)-phenyl ester-co-; -co-[1-[4-(N-ethylenepiperazyl)-4'-nitrostilbene]-N-[(1,1-dimethyl-*m*-isopropenyl)benzyl]]carbamate} : CP-CIHPMI: A vacuum ample was charged with 1.0 g (3.31 mmol), of CIHPMI and 1.74 g (3.31 mmol) of [1-{4-(*N*-ethylenepiperazyl)-4'-nitrostilbene}-*N*-{(1,1-dimethyl-*m*-*iso*prophenyl)benzyl}] carbamate 5.00 mg (0.03 mmol) AIBN (recrystalization from methanol), and 5.00 ml *N*-methylpyrrolidone (NMP). The mother solution was stored at 70° C for 48 hr. The resulting solution was cooled to 25° C. The polymer was precipitated into excess methanol. The solid product was then filtered and washed with methanol. The polymer was purified by repeated precipitation from DMF into methanol, and then THF into n-hexane. It was dried in *vacuo* at 90° C for 48 hr. Percent yield 59.9% (1.64 g).

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Material Processing: For thin film fabrication, the synthesized copolymers were dissolved in tetrahydrofuran (THF)/cyclohexanone. Polymer film was spin coated at 2000 rpm either on indium tin oxide (ITO) precoated glass or normal microslide glass using filtered solution (10 wt.%). When *m*-tetramethyl- xylene diisocyanate (*m* -TMXDI) of the crosslinker was mixed into the polymer solution, the mole ratio of copolymer and crosslinker was set
4 : 1. For photo-curing, we chose the wavelength of 254 nm. The light exposure were maintained during cooling in the presence of the poling field.

Measurement of the Second-order NLO Coefficient d_{33}

The second harmonic generation (SHG) measurements of poled samples were carried out with a Q-switched mode locked, Nd^{+3}:YAG laser operating in the TEM_{00} mode. We followed the standard Maker fringe technique which was already well understood. The second harmonic signal was normalized with respect to that from a calibrated quartz crystal for which value of d_{11}= 0.5 pm/V was assumed.

Measurement of Electro-optic Coefficient, r_{33}

We measured the linear electro-optic coefficients by way of simple reflection technique proposed by C. C. Teng et. al.[9]

RESULTS AND DISCUSSION

Two different class of maleimide copolymers were synthesized, which can be crosslinked either thermally or photochemically. The synthetic procedure were illustrated in scheme 1.

Thermal Cross-link Heterogeneous NLO Structure.: (CP-HPMI with TMXDI)

{1-[4-(N-ethylenepiperazyl)-4'-nitrostilbene]-*N*-[(1,1-dimethyl-isopropenyl) benzyl]}carbamate was synthesized by a reaction of 4-[N-(2-hydroxyethyl) piperazyl]-4'-nitrostilbene with *m*-isopropenyl-α,α-dimethyl benzyl-isocyanate

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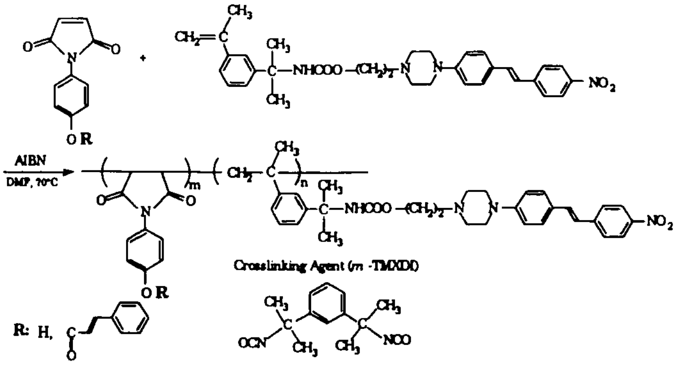

Scheme 1. Synthetic procedure of CP-HPMI and CP-CIHPMI.

(m-TMI) in the presence of catalyst. High reaction yield could be achieved around 70%. The NLO active monomer was copolymerized with either HPMI or CIHPMI through free radical polymerization as depicted in Scheme I. The yield was 44-55% and inherent viscosity was 0.26-0.32 dl/g in DMF at 25°C. The copolymers were quite soluble in common organic solvents such as DMF, THF, and cyclohexanone. With the feeding ratio of 1: 2 (HPMI: NLO monomer), the resultant mole ratio of each component in the copolymer was determined 1 : 0.95, which was estimated by integration of NMR proton signals.

DSC was used to investigate the thermal transition behavior of the copolymer. DSC thermogram showed that these copolymers were amorphous judging from the absence of the melting transition and a high glass transition temperatures appeared. (160°C-203 °C) due to the robust maleimide structure.

In the case of CP-HPMI system, we fabricated the thin film of copolymer and the film with TMXDI and poled the copolymer film with the change of poling field. The EO coefficient, r_{33} increased linearly with the electric field. (see Figure 1) Measured r_{33} value was in the range of 25-30 pm/V at 632.8 nm wavelength when the film was poled under 0.8-1MV/cm at 180°C. SHG measurement was performed to calculate the second-order NLO coefficient, d_{33} value of the poled film. d_{33} value was determined 14 pm/V after corona poling under 5kV at 180°C.

The temporal stability of NLO activity was investigated by monitoring the decay of NLO coefficient as a function of time at elevated temperatures. After being subjected to thermal aging at 80°C for 72 hours, a reduction of only 20 % in the r_{33} value was observed for the poled film.

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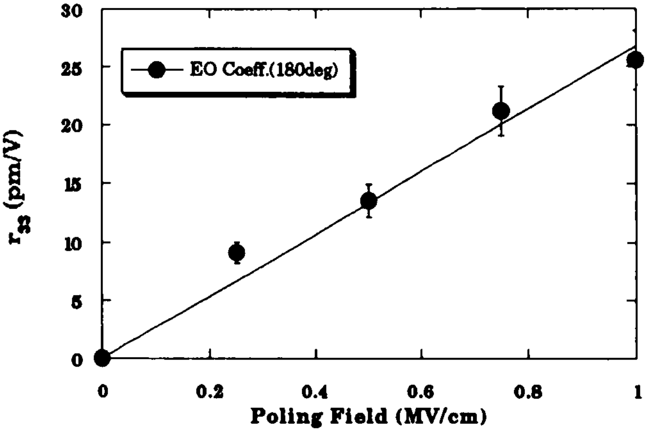

Figure 1. Poling field dependence of r_{33} of CP-HPMI.

After exponential decay of r_{33} at first stage of relaxation, the r_{33} value did not vary at the level of 80% of initial r_{33} value.

The decaying curve of polymer shows two different stages; at first stage, EO coefficient rapidly decreased and then the value slowly decreased and approached to a certain value (~80%) asymptotically at second stage. (see Figure

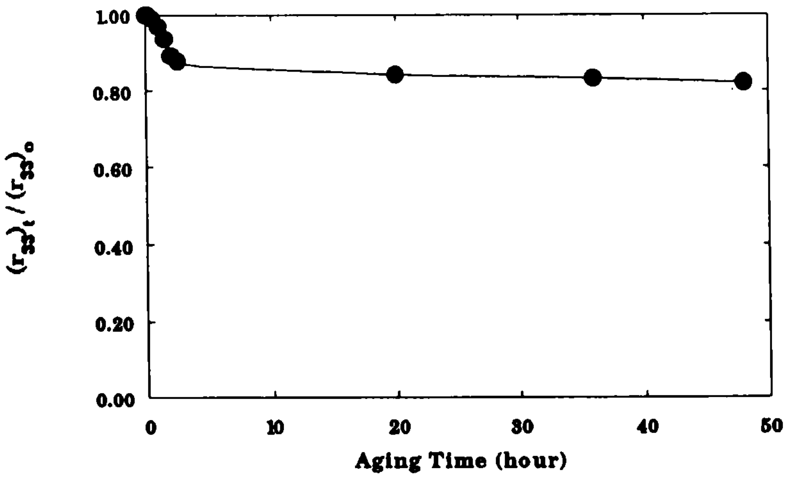

Figure 2. Decaying behaviors of r_{33} in poled CP-HPMI film at 80°C.

2) Therefore, the electro-optic effect of this copolymer was considered quite outstanding resulting from the fairly high EO coefficient and its thermal stability. Based on the theoretical approach, we can fit this data to a

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biexponential of the form, $A\exp(-t/\tau_1) + (1-A)\exp(-t/\tau_2)$. For this case, A = 0.156, τ_1 = 159 minutes, and τ_2 = 120,000 minutes. Therefore, the r_{33} value of this polymer showed the fast decay initially and then decreased very slowly.

During poling, the crosslinking will be induced at the same period. This poling procedure also has a sequential temperature program to pole and then cure the film. We adopted two temperatures, 130°C and 160°C. First, we poled the film at 130°C for 1 hour and then raised the temperature to 160°C gradually in the presence of electric field. After keeping that condition for 1 hour, the poling was completed. Using corona poling method, the UV-VIS spectra of unpoled and poled film of crosslinked polymer were compared. In Figure 3, after two stage poling, the absorption intensity decreased and the absorption peak shifted slightly toward shorter wavelength. Then, the films were aged at 150 °C for 1 hours. Usually, the absorption intensity increases due to randomization of dipolar molecules when aged at high temperature. The film with crosslinking agent showed no change of absorption intensity. Additionally, the solubility of the film was totally different from that before poling. We can believe that the dipolar alignment to poling direction was completely locked up and the stability was quite good upto 150°C. Additionally, it was thought that the copolymer system did not degrade or vaporize throughout the whole period of aging.

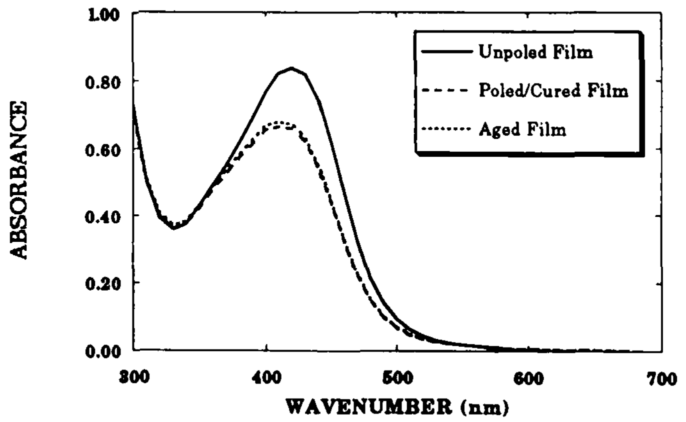

Figure 3. UV-VIS spectra of unpoled, poled and aged film of crosslinked CP-HPMI.

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The FT-IR spectra showed well that the crosslinking reaction between the isocyanate and hydroxyl group in the HPMI occurred. We recorded the FT-IR spectra before curing and after curing at 110°C. We also introduced the difference spectrum of the above two spectra. The IR peaks at 2270cm^{-1} from isocyanate and 3500 cm^{-1} from hydroxyl group decreased after curing. (see Figure 4) This indicates the partial crosslinking reaction occurred through the isocyanate group and the hydroxyl group between the side chains in *p*-hydroxyphenyl maleimide.

Similar to the copolymer film without crosslinker, the EO coefficient, r_{33} of the crosslinked polymer was observed around 25 - 30 pm/V, which depends on the poling field. In an attempt to investigate the temporal stabilities of the films with crosslinker, we aged the sample at elevated temperatures. Aging temperatures were selected 80°C, 100°C, 120°C, and 150°C. We traced the decay of r_{33} over 48 hours at each temperature. The pure copolymer film showed the 80% of the initial value of r_{33} after 2 day aging at 80°C whereas the crosslinked film maintains its r_{33} upto 98% of initial signal over the same period. The crosslinked copolymer showed quite outstanding temporal stability at 80°C compared to the copolymer itself. The crosslinked samples aged at 100°C, and 120°C for 48 hours showed 95% and 90% of the initial EO signal, respectively. Even after 48 hours at 150°C, 80% of the residual signal was remained. (see Figure 5) In the case of photocurable CP-CIHPMI, the electro-optic coefficient was almost consistent with untreated film. We performed the preliminary examination whether the crosslink can be formed under

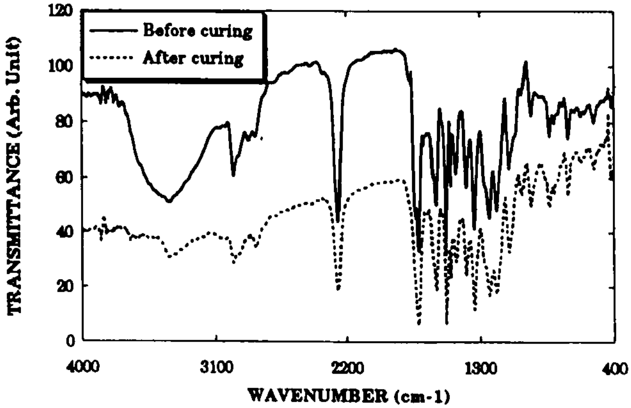

Figure 4. FT-IR spectra of CP-HPMIwith crosslinking agent.
A: Before poling, B: After poling

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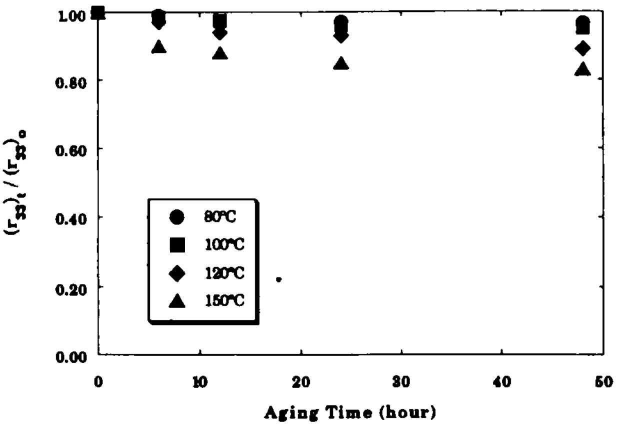

Figure 5. Decay of r_{33} of the crosslinked CP-HPMI under various temperatures.

exposure of 254 wavelength or not. We employed FT-IR spectral analysis using the uncured and cured polymer films. The exposure time was selected 10 minutes and 30 minutes. In Figure 6, the difference of three spectra will be seen ranging from 1800 cm^{-1} and 1400 cm^{-1}. The band at 1638 cm^{-1} can be assigned to be trans alkene of cinnamoyl group. Another alkene bond of stilbene group gave the band at 1608 cm^{-1}. As the exposure time increased, the intensity of the band at 1638 cm-1 decreased. Then for 30 minutes exposure, the band at 1608 cm^{-1} also disappeared simultaneously. This implies that the crosslink reaction between the alkene double bond in cinnamoyl group proceeded under a short exposure time so that the structure will be transformed to cyclized one. Photodimerization was confirmed to be induced under only 10 minutes exposure. Then, after 30 minute exposure, the decomposition of NLO chromphore was thought to be accompanied with the photodimerization. We also confirmed that the EO signal also decreased after long term exposure under 254 nm, wavelength. Regarding the electro-optic coefficient, r_{33}, temporal stability of photocured films was significantly improved, compared to pristine sample. We are making much endeavor to increase the extent of photocrosslink and optimize the poling and curing condition without photobleaching effect.

Shortly, the poling efficiency, hence the resulting second-order NLO activity, the film forming properties, and the temporal stability of poling

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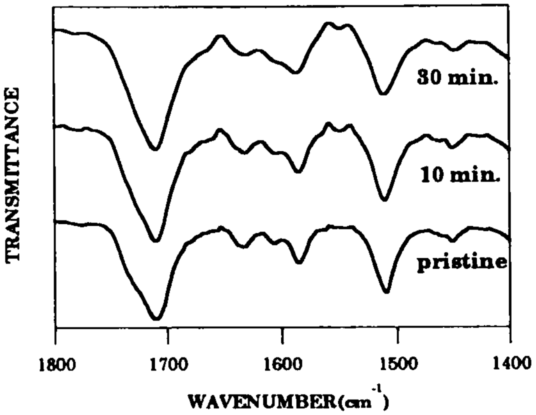

Figure 6. FT-IR spectra of CP-CIHPMI with the change of the exposure time.

induced orientation of these copolymers can be largely enhanced by our synthetic strategy.

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