

Surface Modification by Continuous Graft Copolymerization. III. Photoinitiated Graft Copolymerization onto Poly(ethylene Terephthalate) Fiber Surface

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Synopsis

Photoinitiated grafting is an excellent method to modify the surface properties of a polymer. The presoaking photografting method applied to poly(ethylene terephthalate) (PET) with acrylic acid or acrylamide as monomer using benzophenone as photoinitiator has been investigated. The photografting proceeds under nitrogen atmosphere in a continuous process. The relative intensity of the ESCA lines of nitrogen over carbon of the fiber grafted with acrylamide increased from 3–4% (background) to 8% for 20-s irradiation time. Measured by titration, the amount of grafted poly(acrylic acid) is 0.821 and 1.528 mg/m² with 0.5 M and 2.0 M acrylic acid concentration, respectively, in the presoaking solution at 10-s irradiation time. The dyeability of the fiber, measured by UV absorption, improved. The concentration of initiator and monomer and the solvent used affected the grafting yield. Appropriate conditions promoted photografting of the poly(ethylene terephthalate) fiber. Acetone was a somewhat better solvent than methylethylketone and methylpropylketone.

INTRODUCTION

Recently, surface modification of polymer has received much attention, especially for film and fiber that have a large surface area per unit weight. Among the methods of surface modification, grafting is a promising technology. In principle, graft copolymerization is an attractive method to impart a variety of special functional groups to the surface of a polymer. Graft copolymerization initiated by high-energy irradiation, photoirradiation, or chemical treatment has been well documented. This article deals with grafting of poly(ethylene terephthalate) fiber with acrylamide and acrylic acid photoinitiated by benzophenone in a continuous process.

Poly(ethylene terephthalate) (PET) fibers are highly crystalline and markedly hydrophobic and do not contain chemically reactive groups. To get certain desirable properties, PET can be grafted with such monomers as acrylic acid and acrylamide. Grafting can be accomplished by high-energy radiation, chemical methods, or photoirradiation. Needles et al.¹ studied vapor-phase photografting of methyl acrylate on polyester fiber surface treated with aqueous dispersions of metal oxides. The metal oxides acted either as effective photoini-

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tiators enhancing grafting or as photoabsorbers inhibiting grafting. The irradiation time was 2 h, grafting yield was 0.3–3.4%. Kale et al.² studied the graft copolymerization of acrylic acid and acrylonitrile onto PET fibers and fabric initiated by γ -radiation and benzoyl peroxide. They found that the extent of grafting depended upon irradiation dose, time of reaction, concentration of initiator, and monomer. Seiber and his co-workers³ successfully grafted 2,2,2-trifluoroethyl methacrylate and acrylic acid on polyester by using photoinitiation in a vapor-phase process. Needles et al.⁴ studied photo-induced graft polymerization of methyl acrylate vapor onto polyester fiber when the fiber was wetted with polar solvents. No reports or patents appear in the literature concerning continuous process and short irradiation time up to now. In our previous investigation,⁵ acrylamide and acrylic acid were grafted successfully by the presoaking method onto the surface of high-density polyethylene (HDPE) tape film in a continuous process with short irradiation times. The aim of this work is to study the graft copolymerization of acrylic acid and acrylamide onto PET fiber surface using the continuous process developed.

EXPERIMENTAL

Materials

The poly(ethylene terephthalate) fiber (Terylene Type 125) was obtained from ICI Fibres Co. The decitex/count of the fiber is 1100/192, i.e., tenacity is 77 CN/tex., extension at break is 11.0%, shrinkage (air 180°C) is 15.0%, and shrinkage (water 100°C) is 11.0%. The fiber was thoroughly washed in 60–90°C water containing aqueous detergent for 30 min, then dried prior to use.

Acrylic acid (AA), $\text{CH}_2=\text{CHCOOH}$, MERCK, synthetic grade, 99% (GC), inhibitor of polymerization removed by Al_2O_3 column before use. Acrylamide (AM), $\text{CH}_2=\text{CHCONH}_2$, MERCK, synthetic grade, 99% (GC), recrystallized by acetone once before using. Benzophenone (BP), $\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$, MERCK, synthetic grade, 98% (GC), used without purification. Sodium hydroxide, NaOH, MERCK, Titrisol, 0.01 M. Sodium chloride, NaCl, MERCK, Titrisol, 0.1 M. Acetone, CH_3COCH_3 , MERCK, analytical grade, purity min. 99.5% (GC). Methyl ethyl ketone (MEK=butanone) $\text{C}_2\text{H}_5\text{COCH}_3$, KEBO puriss, min. 99%. Methyl propyl ketone (MPK=pentanone-2), $\text{CH}_3\text{COC}_3\text{H}_7$, MERCK, synthetic grade, purity 98% (GC). Three solvents were used without purification. Crystal violet, $\text{C}_{25}\text{H}_{30}\text{N}_3\text{Cl}$, MERCK, dye indicator for microscopy. UV light source, PHILIPS-HPM 15, high-pressure metal halide lamp with lead and gallium iodide additives. It was made of ozone-free quartz with an activation wavelength between 320 and 440 nm.

Photografting Polymerization Procedure

The device used here was the same as before.⁵ A bundle of polyester fiber is passed through the presoaking solution, then fed into the reactor continuously by turning on the driving motor. The irradiation time of the fiber is 5–170 s by changing the variable motor speed. The reactor is closed and filled with nitrogen during the reaction period. Exhaust gas, including excess nitrogen, vapor of

solvent, monomer, and initiator is vented out from the exhaust outlet. The reaction temperature measured by thermocouple in the reactor, shielded from the UV lamp, is from 68 to 74°C. The vapor of acrylamide is sublimated from solid acrylamide in a vessel under the running roll. The vapor pressure of acrylamide is 0.029 and 2 mmHg at 40 and 87°C, respectively. The distance from the light source to the fabric surface is 20 cm in the experiments. Different monomer and initiator concentrations in the presoaking solution and various solvents have been tested. The time the fiber is contacted with the presoaking solution is about one-third of the irradiation time.

After photografting polymerization, in the case of AM as monomer, the fiber is immersed in acetone for 25–30 min and washed thoroughly to remove residual monomer and initiator, then immersed in hot water (70–90°C) for 25–30 min and washed thoroughly to remove acrylamide homopolymer. In the case of AA as monomer, the fiber is directly immersed in hot water (85–92°C) for 30 min to remove residual monomer and homopoly (acrylic acid) from the surface and finally rinsed with water and dried.

Analysis

ESCA is used for the detection of nitrogen (in amide groups) on the fiber surface. The relative intensity of the ESCA lines N_{1s}/C_{1s} is a measure of the grafting yield. Because the blank PET fiber sample is immersed in the same hot water together with other grafted fiber samples, some homopolymer of acrylamide dissolved in the hot water from the grafted samples contaminated the blank fiber sample. The relative intensity of ESCA lines N_{1s}/C_{1s} of a blank fiber sample is regarded as background.

ESCA analysis is performed with a Leybold Heraeus ESCA/Auger spectrometer LH 2000 unit with a computer on line. As UV absorbance spectrometer for the measurement of ϵ of solvents a Perkin-Elmer spectrophotometer Coleman 575 is used.

A titration analysis method is used here to measure the amount of grafted poly (acrylic acid) on the PET fiber surface. The length of the PET yarn titrated was 20 m with a total surface area of about 0.29 m² (the density of PET fiber is assumed 1.3 g/cm³). The fiber cut in 1–2 cm in length is immersed in 0.1 M sodium chloride solution and stirred for 30 min. pH of the solution is measured by E632 Digital-pH-Meter from Metrohm Ltd., Switzerland. Because the amount of grafted poly (acrylic acid) on the surface of PET fiber is very small, 0.01 M sodium hydroxide solution was used as neutralization agent.

The grafted PET fiber is dyed by immersing in crystal violet aqueous solution, which contains crystal violet 3%, sodium sulfate 5%, and acetic acid 1%, at around 90°C for 75 min, then washed by a detergent solution at 40°C for 30 min, rinsed thoroughly with water, and dried at room temperature. The uptake of crystal violet dye is measured by light absorption at 582 nm. A 0.100-g dyed fiber sample is refluxed in 12 mL acetic acid for 30 min, the solution measured in a Hewlett-Packard 8451 A diode array spectrophotometer. An ungrafted PET fiber is dyed and treated in the same procedure to give the background value of dye absorption.

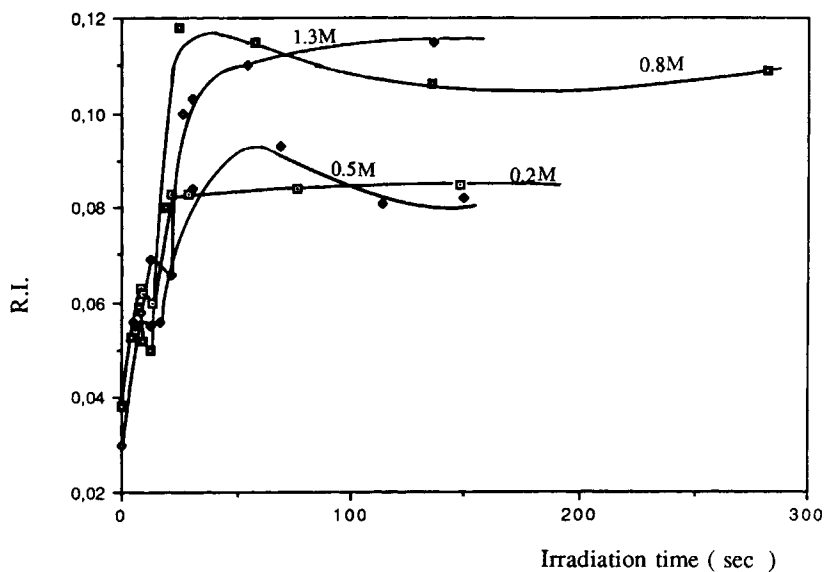


Fig. 1. Effects of monomer concentration on photografting of AM onto PET fiber; presoaking solution: $[BP] = 0.2 M$, acetone as solvent, measured as relative intensity (RI) of ESCA lines N_{1s}/C_{1s} .

RESULTS AND DISCUSSION

Effect of Various Monomer Concentrations in Presoaking Solution

The relative intensity of ESCA lines for different irradiation times and various AM concentrations in the presoaking solution are shown in Figure 1. The relative intensities of ESCA lines were plotted versus irradiation time. All curves in Figure 1 have a "shoulder" from about 10–15 s irradiation time. Monomer

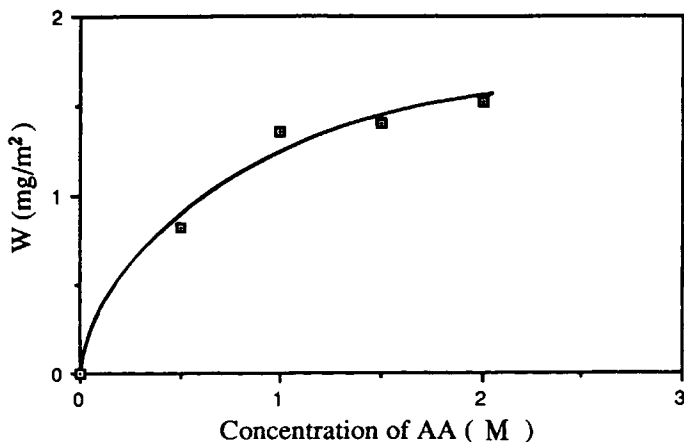


Fig. 2. The amount of grafted poly(acrylic acid) on PET fiber from titration analysis; irradiation time 10 s, presoaking solution $[BP] = 0.2 M$, acetone as solvent.

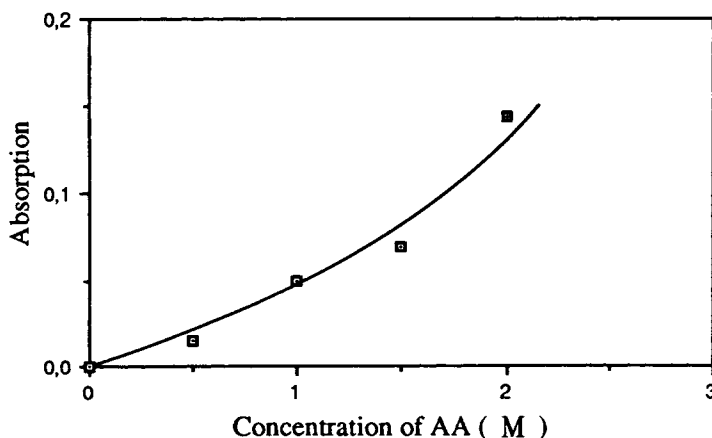


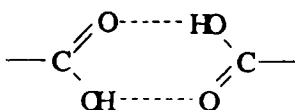
Fig. 3. Dye absorption of grafted PET fiber from aqueous solution of crystal violet; irradiation time 10 s, presoaking solution [BP] = 0.2 M, acetone as solvent.

and initiator molecules are absorbed from the presoaking solution on the fiber surface and react in the grafting reaction.

No further grafting occurred at longer irradiation time (> 30 s) indicating that vapor-phase molecules of initiator and monomer did not react much in the grafting. This may be due to very low concentration of AM and BP in the vapor phase. The titration analysis results (Fig. 2) show that the amount of grafted poly(acrylic acid) on the surface of PET fiber at 10-s irradiation time is a function of the AA concentration in the presoaking solution. This is consistent with the measurements of dye absorption, which are shown in Figure 3.

The higher the AA concentration used in the grafting, the higher is the amount of grafted poly(acrylic acid) on the fiber surface, measured by titration (Fig. 2). From the structure of PET, one mer of PET has one phenyl, two methylenes, and two ester groups. The amount of hydrogen that can be abstracted by the excited photoinitiator molecules per unit surface area is not very high. The grafted poly(acrylic acid) chains formed may be long enough in the case of high AA concentration to cause chain entanglement effect or network structure on the surface layer that probably makes complete neutralization difficult. In addition, hydrogen bonds in the grafted poly(acrylic acid) chains may also partly prevent the neutralization of surface acidity as shown in Scheme 1.

These effects could be reasons for the different tendencies of the curves in Figures 2 and 3. Nevertheless, the level of grafting is related to the concentrations of AM and AA in the presoaking solution.



Scheme 1.

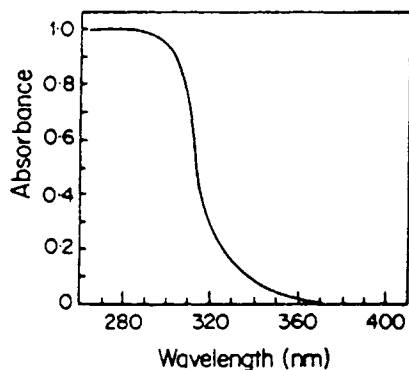


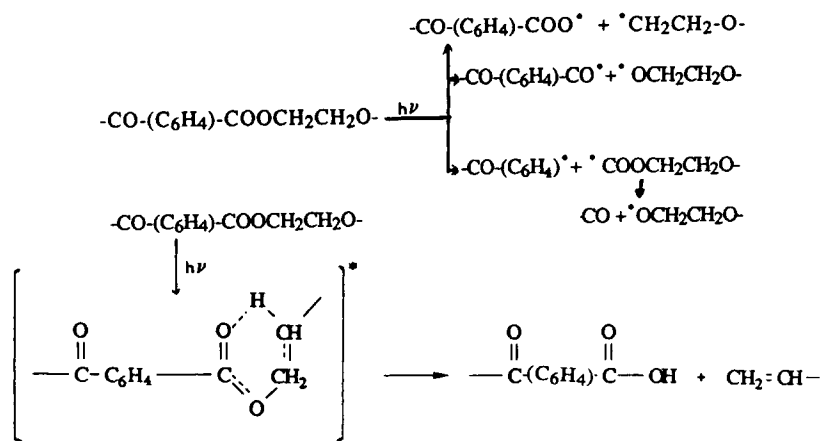
Fig. 4. Absorption spectrum of poly(ethylene terephthalate) [From Osborn, *J. Polym. Sci.*, **38**, 357 (1959)].

The polyester substrate is a bundle of fibers (a yarn) that may trap some oxygen inside to inhibit free radical reactions in grafting. Another factor to consider is that poly(ethylene terephthalate) fibers also absorb UV light, which affects the photodegradation process. The absorption spectrum of PET is presented in Figure 4. UV light is absorbed below 360 nm by the ester carbonyl group chromophores in the polymer and gives radical formation by chain scission after excitation of carbonyl groups to triplet state (a bi-radical) shown in Scheme 2.

It is likely that some of the polyester radicals react with available monomer in the graft polymerization. The grafting reaction was slower for PET, than for PE.⁵ It took about 20 s to get 8% ESCA relative intensity (RI) for PET fiber compared with less 10 s for PE tape film with a final level of RI = 0.10–0.12 for PET and 0.20–0.25 for PE.

Effect of Various Solvents

The relative intensities of ESCA lines N_{1s}/C_{1s} after grafting in various solvents are given in Figure 5.



Scheme 2.

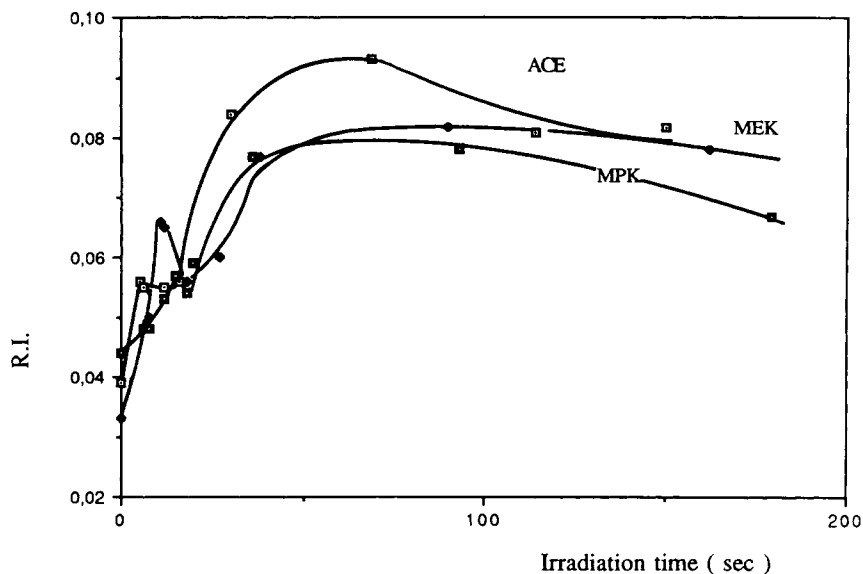


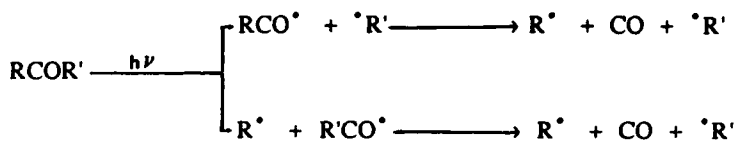
Fig. 5. Solvent effects on photografting of AM onto PET fiber; presoaking solution [AM] = 0.5 M, [BP] = 0.2 M, measured as relative intensity (RI) of ESCA lines N_{1s}/C_{1s} .

The three ketones studied, acetone (ACE), methylethylketone (MEK), and methylpropylketone (MPK), were all active as solvents in the photografting of PET with AM. A shoulder appears at increasing irradiation times (from 5, 10, and 15 s) for the three ketones. This is a further indication that the shoulder is related to the evaporation of the solvents that have increasing boiling point in the same order (for acetone 56.5°C, MEK 79.6°C, and MPK 101.7°C). The ketones have also some UV absorption < 300 nm and may take part in the photochemical initiation. This is related to an $n \rightarrow \pi^*$ transition involving the nonbonding electrons of the oxygen atom in the carbonyl group. The excited carbonyl groups of the solvents may cause a Norrish Type I reaction as shown in Scheme 3.

The molar absorption coefficient ϵ of these three solvents has a maximum at 280 nm (Table I). To what extent the ketone solvent takes part in the grafting reaction is difficult to say. Complex formation with PET and initiator may also occur and influence the initiation. These problems would require a more detailed study.

Effect of Various Photoinitiator Concentrations in Presoaking Solution

The RI of ESCA lines after photografting at different irradiation times and with various photoinitiator concentrations in the presoaking solution are shown



Scheme 3.

TABLE I
Molar Absorption Coefficient (ϵ) of ACE, MEK, and MPK, Heptan
as Solvent, at Room Temperature

	ACE	MEK	MPK
ϵ_{254}	8.1	6.1	6.4
ϵ_{280}	14.9	17.8	19.3

in Figure 6. The shape of the curves in Figure 6 is similar to that in Figures 1 and 5. A shoulder appeared at 5–15 s of irradiation time and may be related to the evaporation of acetone also in this case. The initiator concentrations have only a minor effect on the grafting yield. The grafting yield reached the upper level more rapidly at higher initiator concentrations. Prolonged irradiation time (> 30 s) does not increase the grafting yield further. This is observed in all grafting experiments with PET fiber as substrate polymer.

CONCLUSIONS

Presoaking in a solution of initiator and monomer promotes photografting of AM or AA onto PET fiber surface. Under nitrogen atmosphere and with benzophenone as initiator, short irradiation times in a continuous process give efficient grafting. The dyeability of the PET fibers is improved by photografting with AA as monomer. Measured by titration the amount of poly(acrylic acid) grafted in 10 s is 0.82 and 1.53 mg/m² at 10 s irradiation time in 0.5 M and

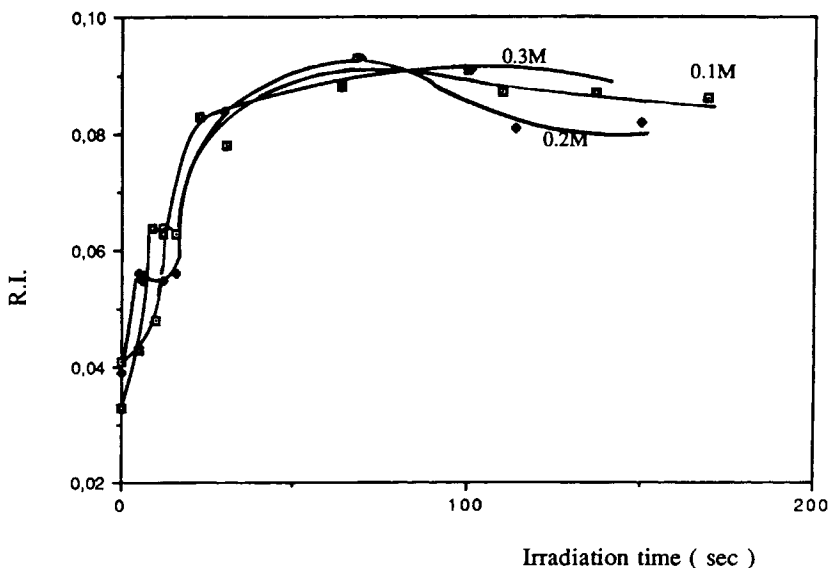


Fig. 6. Effects of photoinitiator concentration on photografting of AM onto PET fiber, presoaking solution $[AM] = 0.5$ M, acetone as solvent, measured as relative intensity of ESCA lines N_{1s}/C_{1s} .

2.0 M AA concentration, respectively, in the presoaking solution. The RI of ESCA lines N_{1s}/C_{1s} of the fiber surface increased from 3–4% (background) to 8–10% in 30-s irradiation time. Compared with PE tape film as substrate polymer, it takes a longer time to graft the PET fiber surface. This is interpreted as due to the difference of the shape between fiber and film and the chemical structure of PET. Increasing concentration of monomer in the presoaking solution gives higher photografting yield. Increasing concentration of initiator had only a minor effect. Acetone as solvent in the presoaking solution gives a higher rate of photografting than MEK and MPK.

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References

1. H. L. Needles and K. W. Alger, *J. Appl. Polym. Sci.*, **19**, 2207–2223 (1975).
2. P. D. Kale and H. T. Lokhande, *J. Appl. Polym. Sci.*, **19**, 461–480 (1975).
3. R. P. Seiber and H. L. Needles, *J. Appl. Polym. Sci.*, **19**, 2187–2206 (1975).
4. H. L. Needles and K. W. Alger, *J. Appl. Polym. Sci.*, **22**, 3405–3418 (1978).
5. P. Y. Zhang and B. Rånby, *J. Appl. Polym. Sci.*, to appear.

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