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SHORT COMMUNICATION

Synthesis of polytetrafluoroethylene/polyacrylate core-shell nanoparticles via emulsifier-free seeded emulsion polymerization

Xuejun Cui · Shuangling Zhong · Jia Xu · Hongyan Wang

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Abstract Polytetrafluoroethylene (PTFE)/polyacrylate core-shell nanoparticles were produced via the emulsifier-free seeded emulsion polymerization of acrylate monomers with PTFE latex as seed. The monomer conversions under different synthesis parameters were monitored by a gravimetric method. The polymerization conditions for preparing PTFE/polyacrylate core-shell nanoparticles were surveyed and optimized. The chemical component of the PTFE/polyacrylate particles was confirmed by comparing the Fourier-transform infrared spectra of PTFE and PTFE/polyacrylate particles. The core-shell structure of the resulting PTFE/polyacrylate nanocomposite particles was investigated by transmission electron microscopy. The water contact angles of the films prepared from PTFE/polyacrylate nanocomposite particles showed that the films were hydrophilic, which confirmed that polyacrylate covered the surface of the PTFE particles. This kind of PTFE/polyacrylate core-shell nanoparticles might advance the compatibility of PTFE with other materials due to the covering of the polyacrylate shell on the surface of PTFE, which would make them promising in various fields.

Keywords Polytetrafluoroethylene (PTFE) · Core shell · Emulsifier-free · Seeded emulsion polymerization · Nanoparticles · Polyacrylate

X. Cui · J. Xu · H. Wang (✉)
Department of Chemistry, Jilin University,
Qianjin Street 2699#,
Changchun 130012, People's Republic of China
e-mail: wang_hy@jlu.edu.cn

S. Zhong
Alan G MacDiarmid Institute,
Department of Chemistry, Jilin University,
Changchun 130012, People's Republic of China

Introduction

Polytetrafluoroethylene (PTFE) is an ideal candidate in widespread applications, such as biomaterials, and chemical, electrical, and mechanical systems [1–4], because of its low frictional coefficient and dielectric constant, few moisture absorption, excellent thermal stability, and chemical inertness [5–7]. These outstanding characteristics are a result of the low polarizability and the high bond energy of the C–F bond (486 kJ/mol), as well as the perfect shielding of the C–C backbone by the fluorine atoms. However, as a counterpart of these remarkable properties, the compatibility and adhesion property of PTFE with other materials are inadequate, which hampers its application in many cases [4, 8], for example, adhesive bonding, lamination, painting, printing, and metallization. Therefore, it is necessary to modify the surface of the PTFE before using PTFE. A great many studies on the surface modification of PTFE have been carried out to enhance its surface functionalities by chemical [9, 10], irradiation [11–13], plasma [14–21], flame [22], corona discharge [23], and ozone treatments [24]. Although these approaches are very useful in offering an opportunity for molecular engineering and design of the PTFE surfaces, they are not easy to bring about because destroying the high bond energy of the C–F bond in the PTFE surface requires a highly reactive chemical [9, 10] or a high-energy input (e.g., plasma or UV) [11–21]. Hence, it is significant to explore a new method that can improve the compatibility of PTFE with other materials without destroying the structure of PTFE.

This aim can be achieved by covering the unmodified surface of PTFE particles with conventional polymers, that is, by forming core-shell particles. Generally, core-shell structure particles are prepared by the emulsion polymerization method. However, the residuary of the emulsifier in materials will greatly influence the purification and performance of the products prepared through traditional emulsion polymerization. To avoid the disadvantages resulting from an emulsifier, attempts have been made by some researchers to prepare emulsifier-free latexes. However, by far, very few papers have reported the preparation and physicochemical characteristics of PTFE-based core-shell particles by emulsifier-free seeded emulsion polymerization method [25–27].

In this study, PTFE/polyacrylate core-shell nanoparticles are synthesized by the emulsifier-free seeded emulsion polymerization of acrylate on the surface of PTFE particles. The resulting PTFE/polyacrylate core-shell nanoparticles can not only keep the PTFE original structure and improve the compatibility of PTFE with other materials but also avoid the disadvantageous effect of the emulsifier on the performance of the products. Accordingly, PTFE/polyacrylate core-shell nanoparticles could adequately display excellent properties of PTFE and are more promising in multifarious application fields. To optimize the polymerization conditions and investigate the structure and properties of PTFE/polyacrylate core-shell nanoparticles, the PTFE/polyacrylate have been characterized by various methods such as Fourier-transform infrared (FTIR) spectrometry, transmission electron microscopy (TEM), dynamic light scattering (DLS) analysis, water contact angles, etc.

Experimental

Materials

Butyl acrylate (BA, 99+%, Aldrich) and methyl methacrylate (MMA, 99%, Aldrich) were distilled under nitrogen atmosphere and reduced pressure before using. Methacrylic acid (MAA, 99%, Aldrich) was used without purification. The acrylate monomers were stored at 5 °C. Ammonium persulfate (APS) and sodium bicarbonate ($NaHCO_3$) were used as received. The PTFE latex (solid content, 60 wt%) was obtained from Shanghai 3F New Materials of China. The water used was distilled followed by deionization.

Preparation of PTFE/polyacrylate core-shell nanoparticles

The PTFE/polyacrylate core-shell latexes were synthesized by the emulsifier-free seeded emulsion polymerization of acrylate with PTFE as seed. All the polymerizations were carried out in a 250-ml four-neck flask equipped with reflux condenser, mechanical stirrer, drop funnel, and inlet for nitrogen gas, and heated in the water bath. The appropriate amount of PTFE latex was introduced into the flask containing 90 ml of deionized water at room temperature with a stirring rate of 300 rpm. The mixture was purged with nitrogen gas, and the nitrogen gas was fluxed continuously during the entire polymerization procedure. The mixture was then heated to 75 °C, and a mixture of BA, MMA, and MAA was added into the flask according to Table 1. After an additional of 30 min equilibration time, an APS aqueous solution (appropriate amount of APS was solved in 10-ml water) was dropped into the above flask, and the final mixture was reacted for 12 h. The obtained latex was purified from the unreacted monomers by repeated dialysis. All the PTFE/polyacrylate latexes were obtained following the above general procedure by varying the amounts of PTFE latex, MAA, and APS. The details of various samples are shown in Table 1.

Characterization

FTIR spectra were recorded on a Nicolet instruments research series 5PC Fourier transform infrared spectrometer. For all samples, KBr pellets were prepared and measured in the range from 4,000 to 400 cm^{-1}.

Transmission electron microscopy (TEM) micrographs were obtained using a JEM-2000 EX transmission electron microscope at an accelerating voltage of 200 kV. The

Table 1 Recipes for the synthesis of PTFE/polyacrylate core-shell nanoparticles

Samples	Core	Shell			APS (g)	$NaHCO_3$ (g)	DI water (g)
	PTFE (g)	MMA (g)	BA (g)	MAA (g)			
Sample 1	0	4.68	4.47	1.015	0.20	0.1	100
Sample 2	3.96	4.68	4.47	0	0.20	0.1	100
Sample 3	3.96	4.68	4.47	0.5075	0.20	0.1	100
Sample 4	3.96	4.68	4.47	1.015	0.20	0.1	100
Sample 5	3.96	4.68	4.47	1.5225	0.20	0.1	100
Sample 6	3.96	4.68	4.47	2.030	0.20	0.1	100
Sample 7	3.96	4.68	4.47	1.015	0.10	0.1	100
Sample 8	3.96	4.68	4.47	1.015	0.15	0.1	100
Sample 9	3.96	4.68	4.47	1.015	0.25	0.1	100
Sample 10	3.96	4.68	4.47	1.015	0.30	0.1	100

samples were prepared by wetting either a carbon-coated or a Formvar-coated grid with a small drop of the dilute latex solution. After drying, they were stained with a small drop of 2% phosphotungstic acid (PTA) for 30 min and dried at room temperature before the test.

The particle sizes (diameters) and their distribution of the PTFE and PTFE/polyacrylate core-shell latexes were measured by a ZetaPALS DLS detector (BI-90Plus, Brookhaven Instruments, Holtsville, NY, USA; 15-mW laser, incident beam = 660 nm) at 25 °C. The scattering angle was fixed at 90°. The samples were highly diluted (C<0.01 wt%) to prevent multiple scattering before testing.

Static contact angles were measured with a JC2000C2 contact angle goniometer (Shanghai Zhongchen Powereach, China) by the sessile drop method at 25 °C. Deionized water was dropped, with a micro-syringe, on the surface of the PTFE sheets or the PTFE/polyacrylate core-shell particles latex films in the atmosphere. The average of the angles obtained at more than ten different locations on each sample surface was reported.

Results and discussion

Effect of the reaction temperature

The energy needed in radical polymeric reaction can be provided by heating the reaction system. Sample 4 is used to exemplify the effects of reaction temperatures on the monomer conversion in the emulsifier-free seeded emulsion polymerization, and the results are shown in Fig. 1. It can be seen from Fig. 1 that when the reaction temperature is 65 °C, the reaction of the acrylate monomers is slow and the final monomer conversion is less than 70%. It is because the initiator APS decomposes so slowly at low temperature that the acrylate monomers are inert to polymerize. As the reaction temperature raises to 75 °C, the decomposing of the initiator speeds and the probability of collision among monomers increases, which lead to the acceleration of the polymerization reaction and the increase of final conversion. When the reaction temperature reaches 85 °C, the final conversion is basically same comparing with that in 75 °C. However, in this high temperature, the polymerization reaction may be too acute and difficult to be controlled due to the quick decomposing of the initiator APS. Hence, the polymerization stability of the emulsion decreases because the heat of reaction cannot be eliminated in time, and even coagulation is inclined to form. To obtain high conversion and excellent production, in this study, we choose 75±1 °C as the reaction temperature of the emulsifier-free seeded emulsion polymerization.

Kinetics of the conversion, average particle size, and polydispersity

Take sample 4 for example. Figure 2 shows the relation of conversion, average particle size, and polydispersity with reaction time. As the polymerization progresses, the conversion increases rapidly in the initial stages and then increases slowly with reaction time and even tends to level off at higher conversion. In these processes, the polyacrylate enwraps on the surface of the PTFE particles and continues to propagate to form the thin shell layer. The thickness of the polyacrylate shell layer grows with the continuous polymerization of acrylate monomers and accumulating of the polyacrylate on the surface of the PTFE particles. That is,

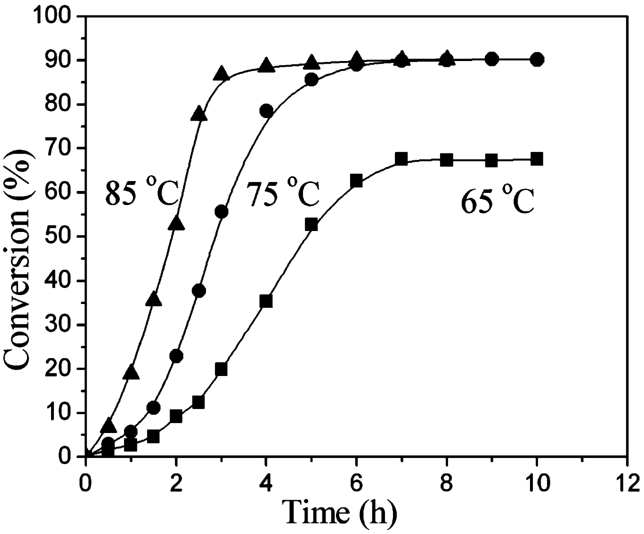

Fig. 1 Effects of reaction temperature on monomer conversion of sample 4

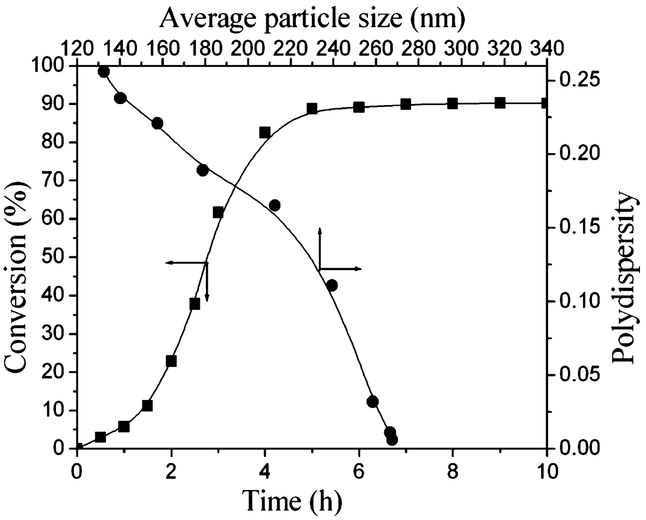

Fig. 2 The conversion, average particle size, and polydispersity of sample 4 as functions of reaction time

the particle size of core-shell particles increases with the increase of monomer conversion (or reaction time). In addition, the polydispersity decreases gradually with the increment of particle size when conversion rises in the polymerization process, which indicates that the distribution of the particle size narrows. In conclusion, when the conversion of the monomers increases with the reaction time, the average particle size enlarges and the particle size becomes more uniform in the emulsifier-free seeded emulsion polymerization.

Effect of the initiator content

The initiator is of vital importance in emulsifier-free emulsion polymerization because it not only initiates the polymerization but also helps to stabilize the latex. During the preparation of core-shell composite particles, initiator ammonia persulphate (APS) decomposes to create free radicals by heating that initiates the polymerization of acrylate monomers. The relatively high concentration of persulphate radicals can speed the polymerization reaction and raise conversion because of the generation of more free radicals per reaction locus per second. It can be seen from Table 2 (sample 4, 7, 8, 9, 10) that when the dosage of APS is lower than 0.2 g, the conversion rises and the polydispersity decreases with the increasing dosage of APS. While the dosage exceeds 0.2 g, the rate of conversion is relatively rapid but the final conversion of samples 9 and 10 are hardly changed comparing with sample 4, and the polydispersity increases. These can be explained based on the fact that when the dosage of APS increases (below 0.2 g), the collision probability among monomers and the particle formation rate increase due to the increase of the radical. However, with the further increase of APS (above 0.2 g), the particles become uneven, owing to the acute collision among monomers that leads to the decrease in the stability of latex. Accordingly, to achieve high conversion and stable uniform particles, a 0.2-g APS is chosen as optimal value for preparing PTFE/polyacrylate core-shell latex when the monomer dosage and concentration of PTFE are fixed.

Table 2 Comparison of the latex and latex film properties

Samples	Conversion (wt%)	Average particle diameter (nm)	Polydispersity	Contact angle (θ)
PTFE	–	127.8	0.060	114.0
Sample 1	95.6	223.8	0.066	56.5
Sample 2	82.3	276.4	0.126	78.0
Sample 3	86.4	264.6	0.082	63.0
Sample 4	90.2	267.5	0.006	56.1
Sample 5	90.5	271.8	0.020	54.5
Sample 6	90.3	270.5	0.077	53.8
Sample 7	81.9	262.1	0.121	61.5
Sample 8	88.2	265.3	0.064	58.4
Sample 9	90.4	267.9	0.109	55.2
Sample 10	90.3	268.7	0.197	54.7

Effect of the amount of MAA

Generally, the hydrophilic monomer tends to locate on the surface of the polymer particles and, therefore, provides stability to the particles in emulsifier-free emulsion polymerization. MAA is more soluble than MMA or BA in water. The colloidal stability can be greatly improved by introducing a small amount of MAA into the polymer particles. It is well known that the function of carboxylic acid monomer is twofold [28]: First, it facilitates the formation of polymer particles, thereby increasing the polymerization rate. Because MAA is soluble in water, aqueous nucleation is a predominant nucleation process in the emulsifier-free emulsion polymerization system [29]. Consequently, with the increment of MAA content, the rate of nucleation and the number of polymerization sites increase, which can cause an increase in polymerization rate and final monomer conversion. Next, it stabilizes the growing particles. The particle can maintain its stability because of the hydrophilic shell provided by the carboxyl groups concentrated at the particle/water interface. In addition, the presence of carboxylic groups chemically bonded to the particles' surface produces some electrostatic repulsion that induces colloidal and mechanical stability of the latexes [28, 30–32]. It can be seen from Table 2 that when the amount of MAA is less than 1.0 g, the monomer conversion increases and the corresponding polydispersity shows a decreasing trend with the increment of MAA content, and the polymerization could be carried out steadily. When MAA content exceeds 1.0 g, a small amount of coagulation generates and the corresponding polydispersity increases, although the reaction could also proceed at a steady rate. Accordingly, the choice of an appropriate MAA amount (1.0 g) can enhance the final monomer conversion and helps to form the monodisperse particles.

FTIR spectra

The FTIR spectra of the PTFE, polyacrylate, and PTFE/polyacrylate particles are showed in Fig. 3. In the FTIR spectrum of PTFE (Fig. 3a), the characteristic absorption peaks of the CF_2 groups at 1,155 cm^{-1} (C–F asymmetric stretching mode) and 1,218 cm^{-1} (C–F symmetric stretching mode), and at the lower wavenumbers of 507 cm^{-1} (CF_2 wagging mode), 548 cm^{-1} (CF_2 deformation mode),

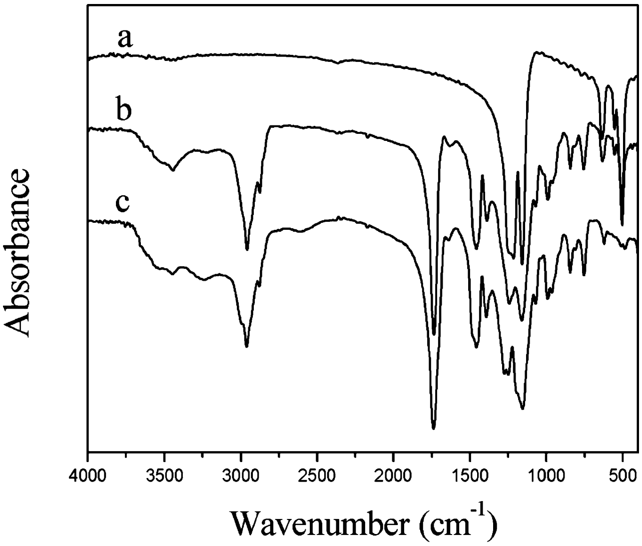

Fig. 3 FTIR spectra of **a** PTFE, **b** PTFE/polyacrylate particles, and **c** polyacrylate particles

and 634 cm^{-1} (CF$_2$ rocking mode) are detected. After polymerizing the acrylate monomers on the surface of the PTFE particles, the FTIR spectrum of the PTFE/polyacrylate particles (Fig. 3b) is different from that of PTFE. The characteristic peaks of PTFE at the lower wavenumbers can still be surveyed in the spectrum of PTFE/polyacrylate particles. However, the characteristic peaks at the range of 1,000–1,300 cm^{-1} are overlapped and enhanced by the C–O–C stretching vibration peaks at 1,240 and 1,157 cm^{-1} of polyacrylate. In addition, the characteristic peaks of the O–H groups at 3,442 cm^{-1}; C–H groups at 2,958, 2,876, 1,455, and 1,386 cm^{-1}; C=O groups at 1,735 cm^{-1}; and C–O–C groups at 1,066 cm^{-1} that originated from polyacrylate are observed in the spectrum of the PTFE/polyacrylate particles. By comparing the FTIR spectra, the formation of PTFE/polyacrylate particles can be confirmed. The core-shell structure of PTFE/polyacrylate particles will be discussed later.

Morphology of the PTFE/polyacrylate core-shell particles

To investigate the microstructure of the PTFE/polyacrylate composite particles, transmission electron microscopy (TEM) is performed, and the TEM micrographs of the PTFE particles and the PTFE/polyacrylate composite particles of sample 4 are showed in Fig. 4. With careful staining of the particles using 2% PTA, the core and shell structures of the composite latex particles can be observed clearly due to the difference of electron penetrability to the core and shell. In Fig. 4b, the light and dark regions in the particles correspond to PTFE and polyacrylate, respectively. That is, compared with Fig. 4a, the PTFE cores (about 130 nm) in Fig. 4b are completely covered by the polyacrylate shells with the thickness of 60–80 nm. This bases on the fact that PTFE is difficult to be swelled due to its high crystallinity [33] that makes the polyacrylate only enwrap on the surface of the PTFE particle and continue to propagate to form the shell layer. The TEM micrograph (Fig. 4b) of the PTFE/polyacrylate particles also shows that the particles are uniform, spherical core-shell particles and have no residual PTFE particles. The average diameters of the PTFE cores and the core-shell particles measured by TEM are consistent with the results measured by the DLS analysis. The average particle diameters of the PTFE cores and the core-shell particles of sample 4 determined by DLS are 127.8 and 267.5 nm, respectively. And the measured diameter of the core-shell particles is closed to the theoretical one (246.2 nm), calculated according to [34]. In addition, the low DLS polydispersity value (0.006) confirms that no secondary nucleation occurs [26, 35]. It is probable that the addition of MAA in polymerization can help to prevent the secondary nucleation and to promote the formation of monodisperse particles [36]. According to the results of TEM and DLS, it can be concluded that the polyacrylate have been enwrapped onto the surface of the PTFE particles and formed monodisperse core-shell particles.

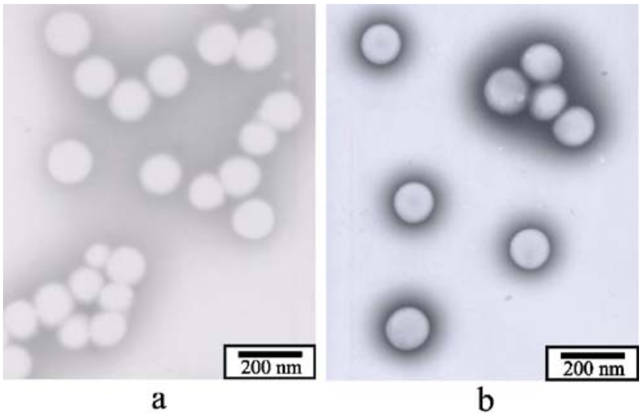

Fig. 4 TEM micrographs of **a** PTFE particles and **b** PTFE/polyacrylate core-shell particles

Hydrophilicity of the PTFE/polyacrylate core-shell particles

Contact angle measurements are taken to observe the hydrophilic/hydrophobic characteristics of films. The effects of the MAA and APS amount on the water contact angles are represented in Table 2. The water contact angle of the pristine PTFE is 114°, showing the hydrophobic behavior of the PTFE surface. After being enwrapped by polyacrylate, the contact angles of all PTFE/polyacrylate samples are less than 90°, meaning that each sample has a hydrophilic surface. It is well known that the hydrophilicity of the material surface depends on its chemical functionality. Here, the hydrophilicity of the PTFE/polyacrylate particles is correlated to the chemical composition and topology of the polyacrylate shell. First, the change of hydrophilicity is much dependent on the formation of hydrophilic groups. After covering polyacrylate on PTFE, hydrophilic groups such as the –(C–O)–, –(C=O)–, and –(C=O)–O– groups are introduced onto the surface of PTFE, which improves the hydrophilicity of the surface. In addition, the hydrophilicity of the PTFE/polyacrylate particles increases with an increasing MAA or APS amount due to the increment of the hydrophilic groups in the polyacrylate shell. However, a few coagulates generate while MAA is beyond 1.0 g, and the particles become uneven if the dosage of the APS exceeds 0.2 g. Thus, the optimal MAA and APS amounts are 1.0 and 0.2 g, respectively. In conclusion, after covering polyacrylate on the surface of PTFE, the hydrophilicity of the surface of PTFE/polyacrylate particles is improved, which will be in favor of improving the compatibility of PTFE with other materials and further facilitate the application of PTFE in many fields.

Conclusion

In this paper, we successfully synthesize PTFE/polyacrylate core-shell nanoparticles by the simple emulsifier-free seeded emulsion polymerization method. The polymerization conditions for synthesizing PTFE/polyacrylate core-shell nanoparticles were investigated and optimized. By the FTIR, TEM, and contact angle measurements, it can be concluded that the PTFE/polyacrylate core-shell nanoparticles have been obtained successfully, and the polyacrylate as shell enwraps on the PTFE core. The TEM micrographs and DLS analysis show that the distributions of core-shell nanoparticles are monodispersed in the latexes. The incorporation of MAA not only improves the stability of PTFE/polyacrylate core-shell latex, but also increases the hydrophilicity of PTFE/polyacrylate core-shell particles. The PTFE/polyacrylate core-shell nanoparticles can keep PTFE's original structure and improve the compatibility of PTFE with other materials. Hence, PTFE/polyacrylate core-shell nanoparticles prepared by this approach could have good prospect and wide application in various fields.

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