Synthesis of aminotelechelic polymers with the redox system $TiCl_3/NH_2OH$ in hydrochloric aqueous phase:
3. Polymerization of methylacrylate. Relation functionality/molecular weight/yield

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(*Received* 17 *March* 1980)

Aminotelechelic poly(methylacrylates) of low molecular weight ($\bar{M}_n < 1.2 \times 10^4$) are prepared with the redox system $TiCl_3/NH_2OH$ in hydrochloric aqueous phase. Functionality, molecular weight and yield are discussed on the basis of initiation, propagation and termination reactions. These considerations justify the influence of several factors (addition time of the $TiCl_3$ solution, molar ratio $MA/TiCl_3$, solvent, nature of the reducing ion...). Gel permeation chromatography confirms the results.

INTRODUCTION

According to some studies[2-4] concerning the polymerization of vinyl monomers initiated with the redox system Ti^{3+}/NH_2OH in the aqueous phase, it appears that the termination step has not been extensively discussed. In a previous paper[1] we developed this point with numerous details. Concerning the polymerization of methylacrylate (MA), we shall assume that the coupling reaction is 100% effective in the termination step[9].

In order to prepare polymethylacrylates (PMA) of low molecular weight ($10^3 < \bar{M}_n < 1.2 \times 10^4$), the following experimental conditions are required: (1) The molar ratio monomer/$TiCl_3 = 10{:}1$; (2) The molar ratio $NH_2OH/TiCl_3 > 1$ in order to minimize secondary reactions[5]; (3) The polymerization solvent:hydrochloric aqueous solution (HCl, N); the water solubility of methylacrylate (about 5% in weight at 25°C [6,7]) allows the reaction to work in a homogeneous medium because the redox system is also soluble in water, but water is a non-solvent of PMA.

The initiation occurs in solution. When the growing chain reaches a given degree of polymerization depending on the chemical affinity, the polymer precipitates in an active state. From the time that two different states coexist for the active macromolecular chains: the first is mobile and in solution, the second is rigid and precipitated. Because of the low mobility of the macromolecular radical in the precipitated state, the termination reactions by coupling are less probable; the life time of the radical is longer and the chain growth increased and therefore high molecular weight polymers are formed. Also, by polymerizing methylacrylate with the redox system Ti^{3+}/NH_2OH in aqueous medium, two types of products are synthesized. The gel permeation chromatography shows a bimodal distribution.

Our purpose is to examine the influence of various parameters on the polymer yield, the molecular weights and the functionality of the aminotelechelic polymers.

EXPERIMENTAL

The experimental methods have been developed previously on the methylmethacrylate polymerization[1]: the results are likewise valid for methylacrylate.

POLYMERIZATION OF METHYLACRYLATE

Influence of the addition time t_1 of the $TiCl_3$ solution

For this study we chose a stirring time, t_2, of 30 min after complete addition of the reducing solution. According to the results of Kakurai *et al.*[3,4], it seems that the polymerization of methylmethacrylate (MMA) is achieved after 30 min of reaction, but methylacrylate polymerizes faster than MMA. Our results are reported in *Table 1*.

Table 1 Influence of the addition time t_1 of $TiCl_3$ solution on the molecular weights ($\bar{M}_n$ and $\bar{M}_w$), the functionality (f) and the polymerization yield. $\bar{M}_n$ and $\bar{M}_w$ values expressed in equivalent of PMMA. Experimental conditions: $MA/TiCl_3 = 10{:}1$, $[MA] = 6 \times 10^{-2}$ mol l^{-1}; $NH_2OH/TiCl_3 = 5{:}1$, $[TiCl_3] = 6 \times 10^{-3}$ mol l^{-1}; $[NH_2OH] = 3 \times 10^{-2}$ mol l^{-1}; temperature: 20°C; $t_2 = 30$ min

t_1	Yield %	$\bar{M}_n$ (g.p.c.)	$\bar{M}_w$ (g.p.c.)	$\bar{M}_w/\bar{M}_n$	f
10 s	50	4750	11 400	2.4	2.1
2 min	78	6550	30 800	4.7	2.0
10 min	45	9450	52 900	5.6	2.1
16 min	45	10 100	175 700	17.4	2.0
40 min	70	11 000	385 000	35	2.0
55 min	65	11 300	429 400	38	2.0

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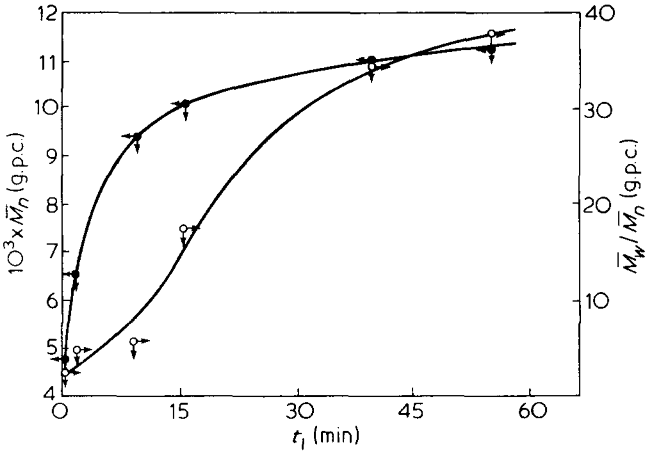


Figure 1 Variations of the number average molecular weight $\bar{M}_n$ and the polydispersity $\bar{M}_w/\bar{M}_n$ as a function of the addition time of $TiCl_3$ solution

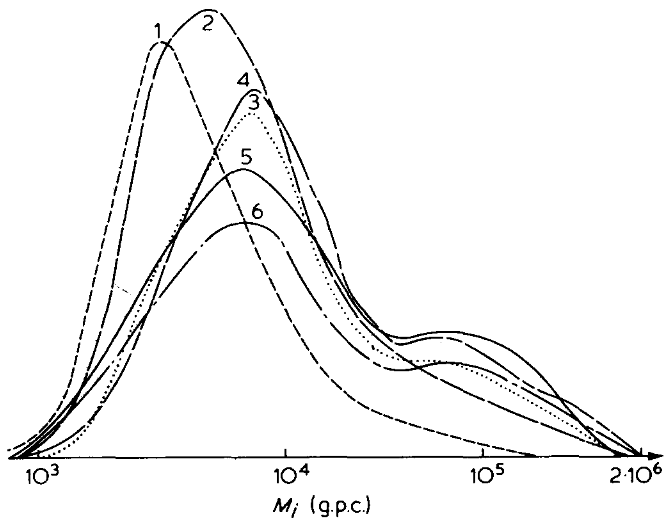


Figure 2 G.p.c. molecular weight distribution of polymers obtained with various addition rates of the $TiCl_3$ solution: (1) 10 s; (2) 2 min; (3) 10 min; (4) 16 min; (5) 40 min; (6) 55 min

Figure 1 shows the evolution of the number average molecular weight $\bar{M}_n$ and the polymolecularity *versus* the addition time t_l of the $TiCl_3$ solution. For a fast addition, the number average molecular weight and the polymolecularity exhibit low values. In order to explain our results, we utilize the hypothesis of Pinazzi *et al.*[8]: the existence of a local overconcentration of radicals. In this zone the overconcentration of initiator favours mostly the initiation reaction at the expense of the propagation, leading to low molecular weight polymers. A slow addition rate of $TiCl_3$ solution causes the values of the number average molecular weight and the polydispersity to increase. Indeed at the beginning of a slow addition, the radical concentration is low in comparison with the fast addition; therefore the possibility of propagation increases and high molecular weight polymers are formed.

The gel permeation chromatograms (*Figure 2*) show a bimodal molecular weight distribution attributable to the coexistence of two different active states of the growing macromolecular chain: —a mobile state (in solution, —a precipitated rigid state. So the precipitated polymer phase leads to high molecular weight compounds whereas the solution polymer phase forms low molecular weight polymers.

The gel permeation chromatograms of polymers obtained for a fast addition rate of $TiCl_3$ present a maximum peak in the low molecular weight range with a slight shoulder appearing in the high molecular weight range. With increasing time of addition of $TiCl_3$ the shoulder develops a peak. However, the amino functionalities are determined using the number average molecular weight and the percentage of nitrogen contained in the polymers. Correct determinations are made on the basis of tonometric $\bar{M}_n$ values relative to polymethylacrylates of low polydispersity.

Alternatively, a good approach is given by using the results relative to some polymethylmethacrylates (*Figure 3*); Serre *et al.*[1] have prepared these polymers at low enough polydispersity in order to determine their $\bar{M}_n$ values by g.p.c. and tonometry. Assuming the relations in *Figure 3* to be valid for our polymethylacrylates, the functionalities calculated from the tonometric $\bar{M}_n$ values (= g.p.c. $\bar{M}_n$ values expressed in equivalent of PMMA) are equal to 2 by disregarding the experimental errors. These results agree well with the conclusion of Bamford and Tipper[9] that the functionality is near 2 owing to the fact that coupling reaction is 100% effective in the termination step.

Influence of the molar ratio MA/$TiCl_3$

Table 2 shows the results and on *Figure 4* we have plotted the number average molecular weight and the

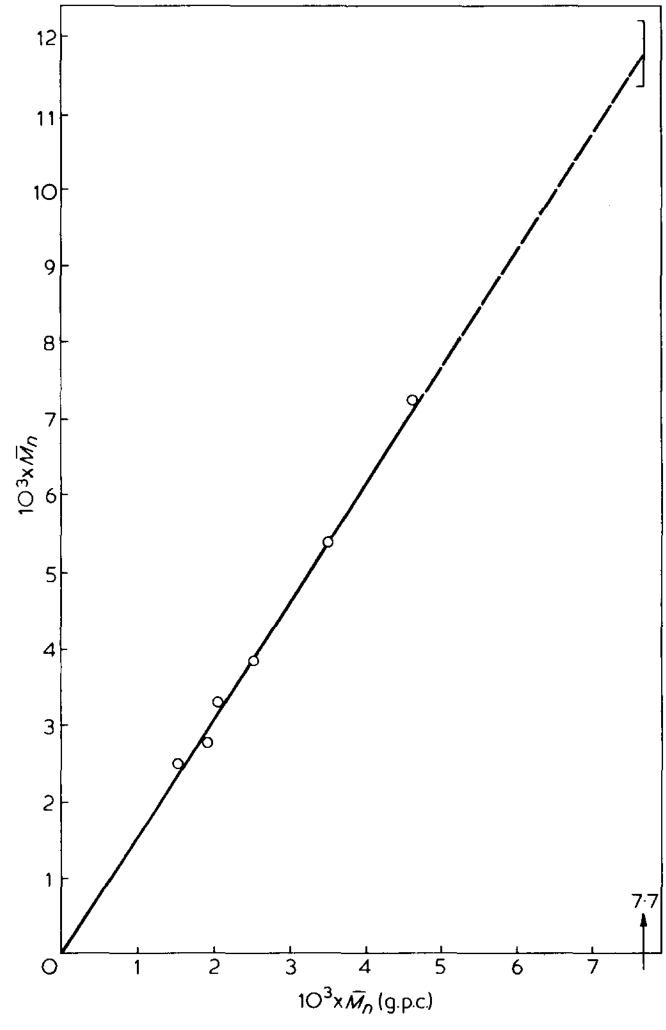


Figure 3 Relation between the number average molecular weights obtained from gel permeation chromatography (g.p.c.) and from tonometric measurements of some poly(methylmethacrylates). A linear relation is supposed for g.p.c.'s weights less than 7700

Table 2 Influence of the molar ratio MA/TiCl$_3$ on the molecular weights ($\bar{M}_n$ and $\bar{M}_w$), the functionality (f) and the polymer yield. The $\bar{M}_n$ and $\bar{M}_w$ values are expressed in equivalents of PMMA. Experimental conditions: [NH$_2$OH] = 3×10^{-2} mol l^{-1}, NH$_2$OH/TiCl$_3$ = 5 : 1; t_1 = 10 s; t_2 = 30 min; temperature: 20°C

MA/TiCl$_3$	Yield %	$\bar{M}_n$ (g.p.c.)	$\bar{M}_w$ (g.p.c.)	$\bar{M}_w/\bar{M}_n$	f
2	54	3400	4800	1.4	2.0
5	40	3900	5800	1.5	2.0
10	50	4700	11 300	2.4	2.1
15	30	6250	29 400	4.7	1.9
35	70	11 500	188 600	16.4	2.1

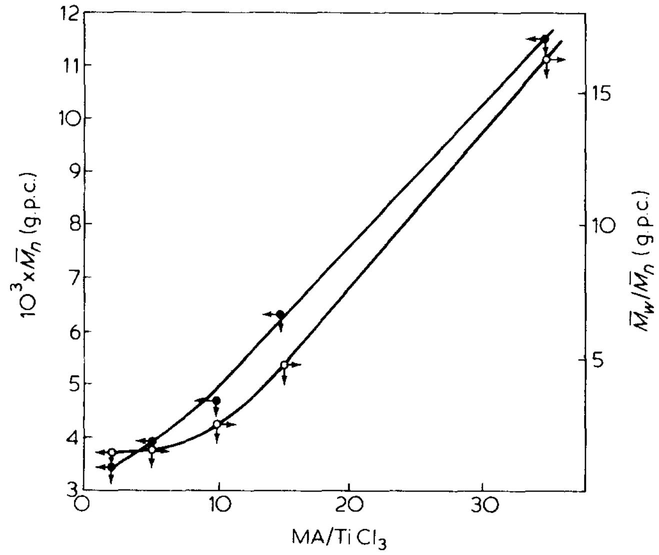


Figure 4 Variations of the number average molecular weight $\bar{M}_n$ and the polydispersity $\bar{M}_w/\bar{M}_n$ in function of the molar ratio MA/TiCl$_3$

polydispersity *versus* the molar ratio MA/TiCl$_3$. Keeping constant the amount of TiCl$_3$ and increasing the monomer concentration, the number average molecular weight and the polydispersity increase with the molar ratio MA/TiCl$_3$. The functionalities determined using *Figure 3*, approach the value 2. When the ratio MA/TiCl$_3$ varies from 2 to 35, high molecular weight polymers are synthesized at the expense of the low molecular weight polymers ones. From a relatively narrow g.p.c. peak (low polydispersity corresponding to the ratio value 2) the chromatograms display a large bimodal distribution (high polydispersity) with increasing ratio MA/TiCl$_3$ (*Figure 5*).

The following explanations justify the results: A low molar ratio MA/TiCl$_3$ corresponds to a high concentration of initiator radicals; in other words, the initiation and the termination reactions by the radical ·NH$_2$ are favoured. A high molar ratio corresponds to an impoverishment of the initiator radicals; this situation favours propagation. As stated before, the bimodal distribution is attributable to the coexistence of two different states of the active propagating chain: a mobile state (in solution) and a rigid precipitated state.

Influence of the molar ratio MA/TiCl$_3$

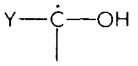
Ti^{3+} is a reducing ion which is about 10^3 times more effective than V^{3+} in the formation of ·NH$_2$ radicals from the system M^{3+}/NH$_2$OH (where M^{3+} = Ti^{3+} or V^{3+}). Less effective ions than V^{3+} are also well known[10]; for instance, several days are necessary to initiate the polymerization of methylmethacrylate using cobalt or iron salts with NH$_2$OH. In the case of V^{3+}, the reaction is almost immediate for a molar ratio MA/VCl$_3$ equal to 1. When the amount of V^{3+} in the reducing solution decreases (the ratio MA/VCl$_3$ increases), the polymerization rate decreases as well. For a ratio equal to 20, the polymer precipitates only after a few minutes.

The variations of the molecular weight and the polydispersity (*Table 3*) are similar in the case of Ti^{3+} and V^{3+}. By decreasing the concentration of the initiator, the propagation is favoured and yields high molecular weight compounds. The evolution of the polydispersity is less pronounced than in the Ti^{3+} study; the g.p.c. chromatograms show this fact (*Figure 6*). The functionalities tend to 2 according to Bamford and Tipper[9].

Influence of the nature of the solvent

All the experiments described above were carried out in aqueous HCl, N phase in order to allow for the homogeneity of the medium, at least until the polymers precipitated. Another reason was to avoid any possible reactions between the ·NH$_2$ radicals and the solvent.

Albisetti *et al.*[10] have studied the reaction between ·NH$_2$ and different solvents. It appears that water does not react with the radical, but methanol, for instance, exhibits different behaviour. Indeed, the photolysis of H$_2$O$_2$ in alcohols leads to radicals like



$$\mathrm{Y{-}\underset{|}{\dot{C}}{-}OH}$$

and yielded by the following reaction[11]:

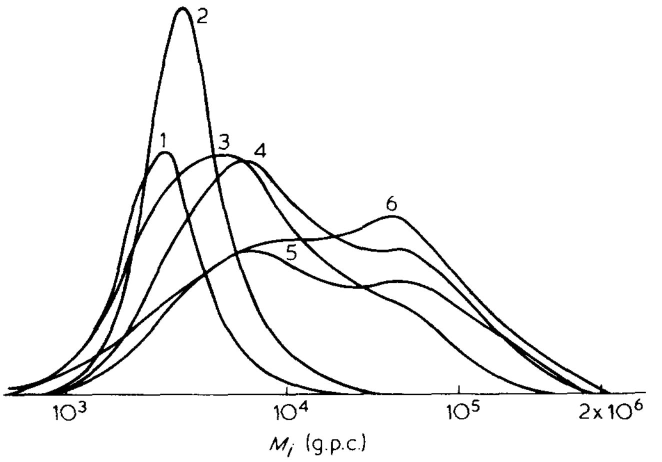


Figure 5 G.p.c. molecular weight distribution of polymers obtained with various molar ratios MA/TiCl$_3$ = R: (1) R = 2; (2) R = 5; (3) R = 15; (4) R = 35; (5) R = 50; (6) R = 80

Table 3 Influence of the molar ratio MA/VCl$_3$ on the molecular weights ($\bar{M}_n$ and $\bar{M}_w$), the functionality (f) and the polymer yield. $\bar{M}_n$ and $\bar{M}_w$ values expressed in equivalent of PMMA. Experimental conditions: NH$_2$OH/VCl$_3$ = 5 : 1; [MA] = 6×10^{-2} mol l^{-1}; t_1 = 15 s; t_2 = 60 min; temperature: 20°C

MA/VCl$_3$	Yield %	$\bar{M}_n$ (g.p.c.)	$\bar{M}_w$ (g.p.c.)	$\bar{M}_w/\bar{M}_n$	f
1	40	7500	42 000	5.6	2.0
3	80	8100	113 400	14	2.1
5	79	8400	201 600	24	2.1
7	78	11 550	311 900	27	2.1
10	75	11 750	352 500	30	2.0

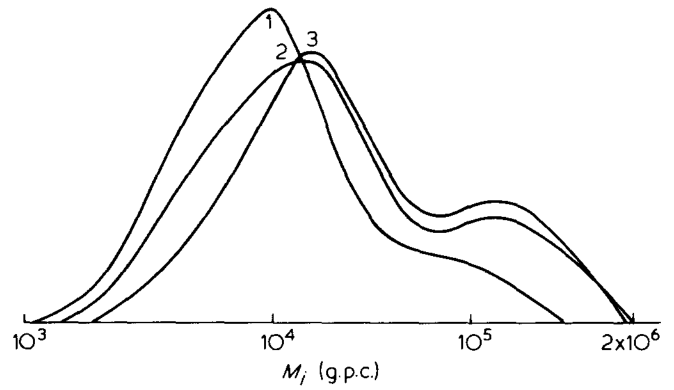
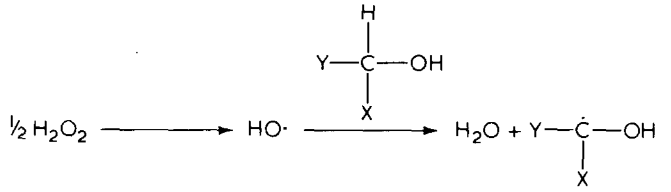


Figure 6 G.p.c. molecular weight distribution of polymers obtained with various molar ratios MA/VCl_3 = *R*: (1) *R* = 1; (2) *R* = 7; (3) *R* = 20



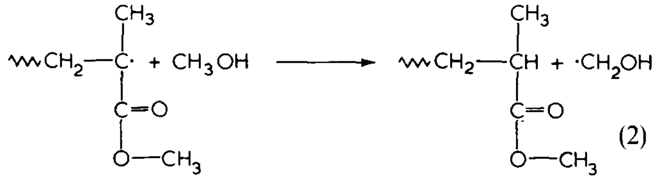
$$\tfrac{1}{2}H_2O_2 \longrightarrow HO\cdot \xrightarrow{Y-\overset{H}{\underset{X}{C}}-OH} H_2O + Y-\underset{X}{\dot{C}}-OH$$

In the case of methanol, the $\cdot CH_2OH$ radicals are able to initiate the polymerization of methylmethacrylate or methylacrylate.

Concerning the polymerization initiated by the system $TiCl_3/NH_2OH$ in methanolic phase, it is not unreasonable to suppose that the following reaction takes place:

$$CH_3OH + \cdot NH_2 \rightarrow \cdot CH_2OH + NH_3 \qquad (1)$$

The above hypothesis is supported by the fact that transfer reactions are possible from the growing active chain to methanol:



$$\sim\!\!\sim CH_2-\overset{CH_3}{\underset{C(=O)-O-CH_3}{C\cdot}} + CH_3OH \longrightarrow \sim\!\!\sim CH_2-\overset{CH_3}{\underset{C(=O)-O-CH_3}{CH}} + \cdot CH_2OH \qquad (2)$$

These considerations are quite satisfactory to justify the notable decreasing of the number average molecular weight and the aminofunctionality when methylacrylate or methylmethacrylate are polymerized with the system $TiCl_3/NH_2OH$ in hydrochloric aqueous phase and in methanol respectively (*Table 4*). The decrease of $\bar{M}_n$ is explained by reactions (1) and (2). The extremely low aminofunctionality observed for PMA and PMMA is directly related to reaction (1).

CONCLUSIONS

We have synthesized some aminotelechelic polymethylacrylates of low molecular weights ($10^3 < \bar{M}_n < 10^4$) using the catalytic system $TiCl_3/NH_2OH$ in hydrochloric aqueous phase. At a given time two kinds of growing active chains coexist in the medium: one in solution and one precipitated.

In the precipitated state the termination by coupling seems less probable and the longer lifetime of the radical favours the propagation step and high molecular weight polymers are formed. To the contrary, in solution the possibility of termination by coupling is enhanced, leading therefore to low molecular weight polymers being formed. A local overconcentration in $\cdot NH_2$ radicals favours the initiation at the expense of the propagation and allows an increased possibility of termination by the radicals themselves so that low molecular weight compounds are obtained. Increasing the addition rate and/or the dilution of $TiCl_3$ suppress(es) the local over concentration of $\cdot NH_2$ radicals and allows the formation of high polymers.

Table 4 Influence of methanol on the aminofunctionality of polymethylacrylates (PMA) and polymethylmethacrylates (PMMA) obtained with the redox system $TiCl_3/NH_2OH$. $\bar{M}_n$ values expressed in equivalent of PMMA. Experimental conditions: MA/Ti^{3+} = 10:1; MMA/Ti^{3+} = 10:1; t_1 (MA in HCl, N): 16 min; t_1 (MMA in HCl, N): 60 min; t_1 (MA in methanol): 20 min; t_1 (MA in methanol): 60 min

Polymer	Solvent	$\bar{M}_n$ (g.p.c.)	*f*
PMMA	HCl, N	6550	1.8
	methanol	1050	0.1
PMA	HCl, N	10100	2.0
	methanol	2550	0.3

These considerations are reasonable enough to justify the influence of parameters like the addition rate of $TiCl_3$, the molar ratio MA/$TiCl_3$ and so on. The results are supported by gel permeation chromatography analysis.

The termination reactions by coupling of two macromolecular growing chains and by $\cdot NH_2$ radical addition lead to aminotelechelic polymers whose functionality approaches the value 2. This result has been verified for some number average molecular weights $\bar{M}_n$ less than 7700. ($\bar{M}_n$ determined by g.p.c. and expressed in equivalent of PMMA.)

When methanol is used as the solvent, the radical $\cdot NH_2$ does not increase the initiation of the polymerization; the transfer reaction to methanol is favoured and the $\cdot CH_2OH$ radical formed is able to induce the polymerization and the amino functionality drops drastically.

ACKNOWLEDGEMENTS

The authors are greatly indebted to the ELF–ERAP company. This work was entirely supported by the grant no 2155. The authors would also like to thank Jean-Pierre Ferrand for his technical assistance.

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