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Polymer 40 (1999) 807–811

polymer

Polymer Communication

Polymerization of acrylamide in the presence of peroxodisulfate and ultrasound

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Received 5 December 1997; revised 25 February 1998; accepted 13 March 1998

Abstract

Polymerization of acrylamide was specifically performed under conditions wherein no polymerization could occur in the absence of ultrasound and initiator. Polymerizations were carried out in the presence of peroxodisulfate and ultrasound. The rate of polymerization and the rate of peroxodisulfate disappearance were followed under various conditions to arrive at the rate dependencies. The observed results were adequately explained in terms of the proposed mechanism. The rate parameters were evaluated and provided as evidence for the polymerization which can occur in the presence of ultrasound. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Polymerization; Acrylamide; Peroxodisulfate

1. Introduction

Peroxodisulfate (PDS) has been employed as a mild oxidising agent [1] and as an initiator for the polymerization of vinyl monomers. In particular, PDS was used as a lone initiator for the polymerization of acrylamide [2,3], although a suitable reaction scheme to justify the experimental results was not proposed. This prompted our earlier group to reinvestigate the polymerization of acrylamide in detail [4] in a nitrogen atmosphere. Polymerization was also extended using an acid salt of PDS, peroxomonosulfate (PMS), for the polymerization of acrylamide [5]. PDS has also been used in a redox couple for vinyl polymerization [6]. The radicals capable of initiating vinyl polymerization were usually produced by thermal or photochemical decomposition of either the pure monomer or the added initiator component. The possibility of using ultrasound to initiate polymerization was explored for polyacrylonitrile formation in aqueous solution [7], and Price et al. [8] used ultrasound to initiate polymerization of methyl methacrylate. Clearly, from these studies [7,8], if the ultrasound method could be applied to initiate vinyl polymerization, it would provide an alternative method of initiation with the possibility of obtaining a great deal of control over the process; hence, ultrasonic initiation may produce polymers with predetermined structures and properties, such as molecular weight, polydispersity and tacticity. In the presence of ultrasound the polydispersity is altered due to the following combined effects. The enhanced molecular motion and possibility of initiation occurring evenly throughout the system through mixing to produce more chains at the same rate are the factors to cause changes in polydispersity [9]. The manipulation of the experimental conditions, namely the temperature and ultrasound intensity, allows the preparation of polymers with controlled molecular weight and tacticity [8]. For example, high frequency, low intensity ultrasound has been used for following the course of polymerization reactions [10] and for monitoring conformational changes in polymers [11]. In the present study, experimental conditions were employed in such a way that polymerization could not occur in an aqueous solution of acrylamide alone in the presence of ultrasound. Recently Price and Clifton [12] studied in detail the kinetics of decomposition of PDS in the presence of ultrasound and projected the possibility of using such decomposition for initiating vinyl polymerization at ambient temperatures. This triggered us to investigate the polymerization dynamics of aqueous acrylamide solution in the presence of PDS as initiator using ultrasound. The present investigation was hence directed at monitoring the course of polymerization of acrylamide in the presence of ultrasound and PDS and to elucidate the plausible mechanism for the polymerization.

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PII S0032-3861(98)00230-4

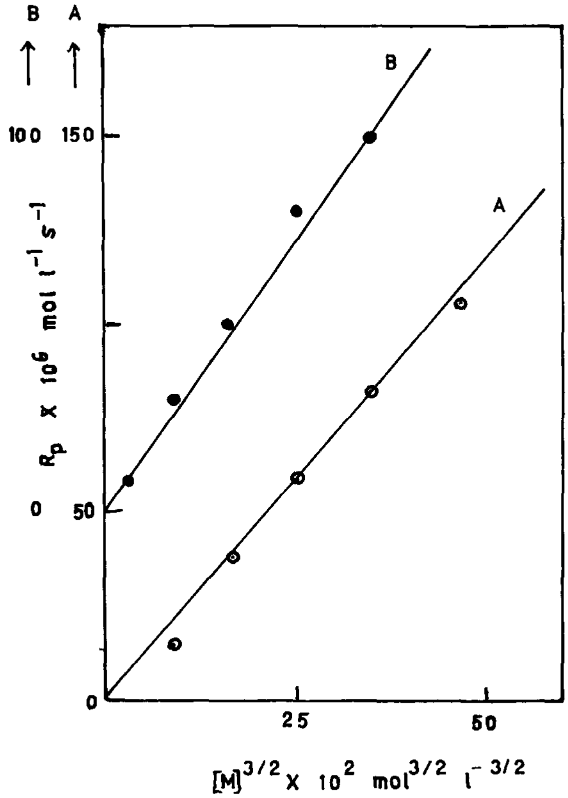

Fig. 1. Dependence of R_p on acrylamide concentration in the presence of ultrasound of frequency 1 MHz at 35°C: (A) [PDS] = 8.40×10^{-3} mol l^{-1}; (B) [PDS] = 10.5×10^{-3} mol l^{-1}.

2. Experimental

Potassium peroxodisulfate (E. Merck, AR) was used as supplied. Acrylamide (American Cyanamide) was recrystallized from chloroform [13]. All other reagents were of Analar grade and used without further purification. Water, doubly distilled over alkaline permanganate in an all-glass apparatus, was used for preparing all solutions after purification by deionizing.

Solutions of acrylamide monomer (M) and the initiator (PDS) were prepared daily afresh and estimated by bromometry [14] and iodometry, respectively. Polymerization was carried out in a thermostat cell (12 ml capacity) of an ultrasonic interferometer (M/s. Mittal Enterprises, Delhi, India) which can impart ultrasound of frequency 1 MHz (intensity 0.7 mW cm^{-2}) to the reaction solution. A solution of the requisite amount of acrylamide was taken in the cell and water was circulated through the outer jacket of the cell using a thermostat (M/s. Toshniwal Brothers, India) maintained at a predetermined temperature with an accuracy of 0.1°C . A pre-equilibrated PDS solution of the requisite volume was added to the cell and the total volume of the reaction system was maintained at 10 ml. The time of passing the ultrasound was taken as the starting time for the polymerization. The rate of polymerization, R_p (− d[M]/d*t*), was determined by monitoring the concentration of unreacted monomer at the polymerization time by bromometry [14] and the rate of PDS disappearance (−d[PDS]/d*t*) was followed for the polymerization conditions simultaneously by estimating the concentration of unreacted PDS by iodometry.

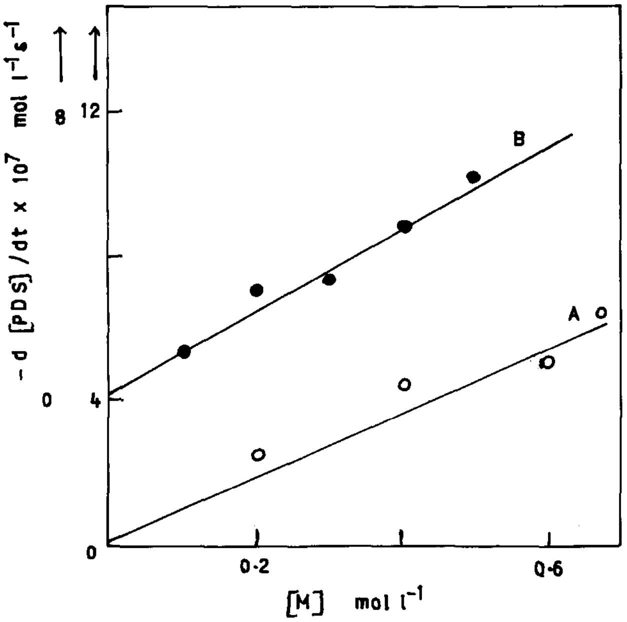

Fig. 2. Dependence of − d[PDS]/d*t* on acrylamide concentration in the presence of ultrasound of frequency 1 MHz at 35°C: (A) [PDS] = 8.40×10^{-3} mol l^{-1}; (B) [PDS] = 10.5×10^{-3} mol l^{-1}.

3. Results and discussion

Trial experiments were carried out for various concentrations of acrylamide monomer and PDS initiator in the absence of ultrasound and it was found that there was no polymerization when these experimental conditions were employed. Polymerization was, however, observed in the presence of ultrasound under specific conditions only with PDS as added initiator. All the polymerization studies were carried out with these conditions. The rate of polymerization was followed for [M] in the range (0.2–0.6 mol l^{-1}) while keeping [PDS], temperature and the frequency of the ultrasound constant. The linear nature of the plot of R_p versus $[M]^{3/2}$ (Fig. 1A) gave an indication that R_p showed a 3/2-order dependence on [M]. Additional experiments under a different set of experimental conditions also confirms the above fact and this is evident from Fig. 1, plot B. Under the above conditions, − d[PDS]/d*t* was also followed simultaneously and found to have a first-order dependence −d[PDS]/d*t* on [M]. The plots of −d[PDS]/d*t* versus [M] (Fig. 2A,B) were found to be linear with negligible intercept suggesting the first-order dependence of the monomer.

The concentration of PDS was varied in the range ($6–12 \times 10^{-3}$ mol l^{-1}) and R_p was determined and found to have a linear dependence on $[PDS]^{1/2}$ (Fig. 3A).

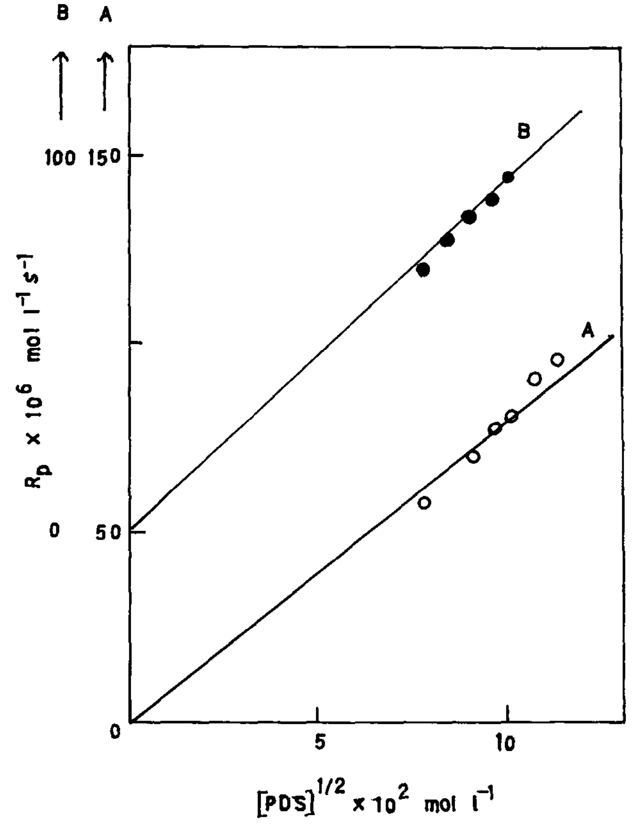

Fig. 3. Dependence of R_p on PDS concentration in the presence of ultrasound of frequency 1 MHz at 35°C: (A) [M] = 0.4 mol l^{-1}; (B) [M] = 0.5 mol l^{-1}.

Experiments with a set of different conditions also favoured such a square root dependence of [PDS] on R_p (Fig. 3B).

The value of $-$ d[PDS]/dt was found to increase with [PDS] under both the above experimental conditions. A first-order dependence was inferred from the linear plot of $-$ d[PDS]/dt versus [PDS] (Fig. 4A,B).

Polymerization was carried out in the presence of ultrasound with different temperatures. R_p and $-$ d[PDS]/dt were found to show a steady increase with temperature in both parameters.

A plausible mechanism is attempted for the acrylamide polymerization to account for the above experimental results. PDS decomposition and consequent reaction of the generated sulfate ion radical, $SO_4^{\cdot-}$, with monomer was reported as a probable initiation for the polymerization. In the present study, a clear first-order dependence of $-$d[PDS]/dt on [M] (Fig. 2) indicated the direct involvement of the monomer in the initiation. This would obviously mean the following alternative type of reaction as initiation:

$$PDS + M \rightarrow M_1^{\cdot} + SO_4^{\cdot-}$$

This type of initiation was earlier observed in the aqueous thermal polymerization of acrylamide [4]. However, the same reaction would happen with a different rate in the presence of ultrasound. Keeping this in view, and also the observed square root dependence of R_p on [PDS], the following mechanistic scheme is proposed for acrylamide polymerization in the presence of ultrasound and PDS:

$$PDS + M \xrightarrow{k_1} M_1^{\cdot} + SO_4^{\cdot-} \qquad (1A)$$

$$SO_4^{\cdot-} + H_2O \xrightarrow{k_2} {}^{\cdot}OH + HSO_4^{-} \qquad (1B)$$

$${}^{\cdot}OH + M \xrightarrow{k_3} M_1^{\cdot 1} \qquad (2)$$

$$M_1^{\cdot} + M \xrightarrow{k_p} M_2^{\cdot} \qquad (3)$$

$$M_1^{\cdot 1} + M \xrightarrow{k_p} M_2^{\cdot 1}$$

$$M_{n-1}^{\cdot} \ (\text{or } M_{n-1}^{\cdot 1}) + M \xrightarrow{k_p} M_n^{\cdot} \ (M_n^{\cdot 1})$$

$$M_n^{\cdot} \ (M_n^{\cdot 1}) + M_n^{\cdot} \ (M_n^{\cdot 1}) \xrightarrow{k_t} \text{Polymer} \qquad (4)$$

where $M_1^{\cdot 1}$ = HO–CH$_2$–C$^{\cdot}$H–CONH$_2$ and $M_1^{\cdot}$ = $^{-}$SO$_4$–CH$_2$–C$^{\cdot}$H–CONH$_2$.

Assuming steady state conditions for all the radicals present, the following relations are derived:

$$R_p = \sqrt{2}(k_p/k_t^{1/2})[M]^{3/2}[PDS]^{1/2} \qquad (5)$$

$$-\,d[PDS]/dt = k_i[M][PDS] \qquad (6)$$

These above-derived expressions are consistent with our experimental observations such as the 3/2-order dependence of R_p on [M] (Fig. 1), the square root dependence of R_p on [PDS] (Fig. 3) and the first-order dependence of [M] and [PDS] on $-$ d[PDS]/dt (Figs 2 and 4).

3.1. Evaluation of rate constant

The choice of Eq. (5) as an expression for R_p and Eq. (6) for $-$ d[PDS]/dt can be tested by evaluation of rate parameters. From the slope of the plots of R_p versus $[M]^{3/2}$ (Fig. 1) and R_p versus $[PDS]^{1/2}$ (Fig. 3), $(k_p/k_t^{1/2})k_i^{1/2}$ was evaluated and is presented in Table 1. The consistency of the values obtained under different experimental conditions can be seen in the table and justified the proposed mechanism and Eq. (5) as the choice of expression for R_p. The average value of this composite rate constant is found to be 1.8 × 10^{-3} s^{-1} at 35°C.

From the slopes of $-$ d[PDS]/dt versus [M] and $-$d[PDS]/dt versus [PDS], the k_i values were calculated and are given in Table 1. The average value was found to be 14.2 × 10^{-5} mol l^{-1} s^{-1}. It is now worthwhile to compare this k_i value now obtained and the rate constant of the simple decomposition of PDS reported [12] by earlier workers (1 × 10^{-7} s^{-1}). The higher k_i value in the present case in combination with the linear nature of the plot of R_p versus

Table 1
Evaluation of rate constants for acrylamide polymerization in the presence of ultrasound of frequency 1 MHz at 35°C

$[M] \times 10\,\mathrm{mol\,l^{-1}}$	$[PDS] \times 10^{3}\,\mathrm{mol\,l^{-1}}$	Slope	k^*	k_i	$(k_p/k_t^{1/2})$
Varied over a range	8.4	$1.00 \times 10^{-6}\,\mathrm{s^{-1}}$	—	$11.9 \times 10^{-5}\,\mathrm{mol^{-1}\,l\,s^{-1}}$	—
	10.5	$1.25 \times 10^{-6}\,\mathrm{s^{-1}}$	—	$11.9 \times 10^{-5}\,\mathrm{mol^{-1}\,l\,s^{-1}}$	—
	8.4	$2.32 \times 10^{-4}\,\mathrm{mol^{-1/2}\,l^{1/2}\,s^{-1}}$	$1.78 \times 10^{-3}\,\mathrm{s^{-1}}$	—	$0.16\,\mathrm{mol^{-1/2}\,l^{1/2}\,s^{-1/2}}$
	10.5	$2.70 \times 10^{-4}\,\mathrm{mol^{-1/2}\,l^{1/2}\,s^{-1}}$	$1.87 \times 10^{-3}\,\mathrm{s^{-1}}$	—	$0.17\,\mathrm{mol^{-1/2}\,l^{1/2}\,s^{-1/2}}$
4.0	Varied over a range	$6.50 \times 10^{-5}\,\mathrm{s^{-1}}$	—	$15.0 \times 10^{-5}\,\mathrm{mol^{-1}\,s^{-1}}$	—
5.0		$9.00 \times 10^{-5}\,\mathrm{s^{-1}}$	—	$18.0 \times 10^{-5}\,\mathrm{mol^{-1}\,l\,s^{-1}}$	—
4.0		$7.80 \times 10^{-4}\,\mathrm{mol^{-1/2}\,l^{1/2}\,s^{-1}}$	$2.18 \times 10^{-3}\,\mathrm{mol^{-1}\,l\,s^{-1}}$	—	$0.18\,\mathrm{mol^{-1/2}\,l^{1/2}\,s^{-1/2}}$
5.0		$8.40 \times 10^{-4}\,\mathrm{mol^{-1/2}\,l^{1/2}\,s^{-1}}$	$1.68 \times 10^{-3}\,\mathrm{mol^{-1}\,l\,s^{-1}}$	—	$0.16\,\mathrm{mol^{-1/2}\,l^{1/2}\,s^{-1/2}}$

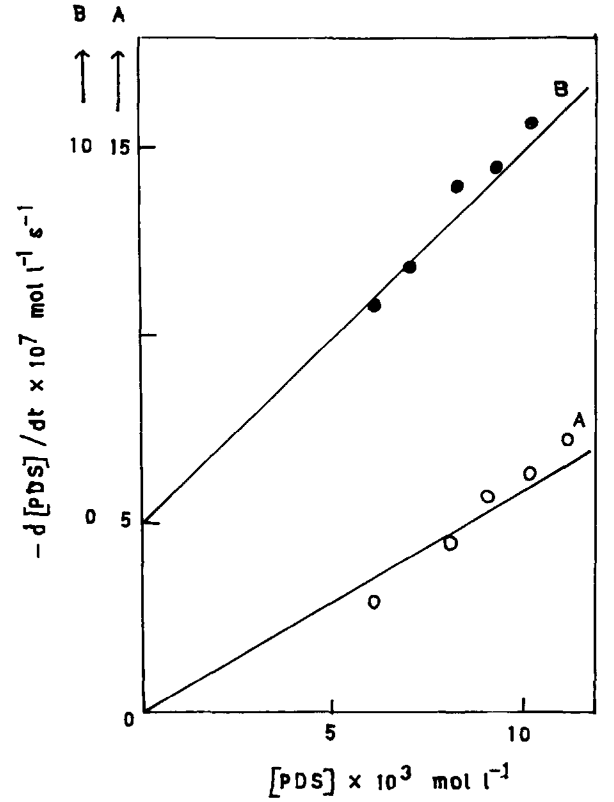

Fig. 4. Dependence of $-\,d[PDS]/dt$ on PDS concentration in the presence of ultrasound of frequency 1 MHz at 35°C: (A) $[M] = 0.4\,\mathrm{mol\,l^{-1}}$; (B) $[M] = 0.5\,\mathrm{mol\,l^{-1}}$.

$M]^{3/2}$ rules out the initiation by

$$S_2O_8^{2-} \rightarrow 2SO_4^{\cdot -}$$

$$SO_4^{\cdot -} + M \rightarrow M_1^{\cdot}$$

where $M_1^{\cdot} = {}^{-}SO_4\text{–}CH_2\text{–}C^{\cdot}HCONH_2$.

In addition to this, the average k_i value here, is found to be even higher ($14.2 \times 10^{-5}\,\mathrm{mol\,l^{-1}\,s^{-1}}$) than the rate constant for the reaction

$$PDS + M \rightarrow M_1^{\cdot} + SO_4^{\cdot -}$$

reported in earlier work [4] for thermal polymerization ($5.46 \times 10^{-7}\,\mathrm{mol\,l^{-1}\,s^{-1}}$). These observations favour Eq. (1A) and Eq. (1B) as initiation reactions in the presence of ultrasound. Hence, a faster rate of production of primary radicals and $M_1^{\cdot}$ is expected. The mechanism of thermal decomposition of PDS is believed to produce the sulfate ion radical which can abstract a hydrogen from water to give hydroxyl radicals. Either of the radical species can, in principle, act as initiator [15]. Later, through photolytic studies on the decomposition of PDS [16], it was confirmed that the sulfate ion radical primarily formed [17] reacted rapidly with water to yield hydroxyl radicals. In the present study, the k_i value for the ultrasonic initiation is far higher than for the thermal initiation [4]. Obviously an accelerated

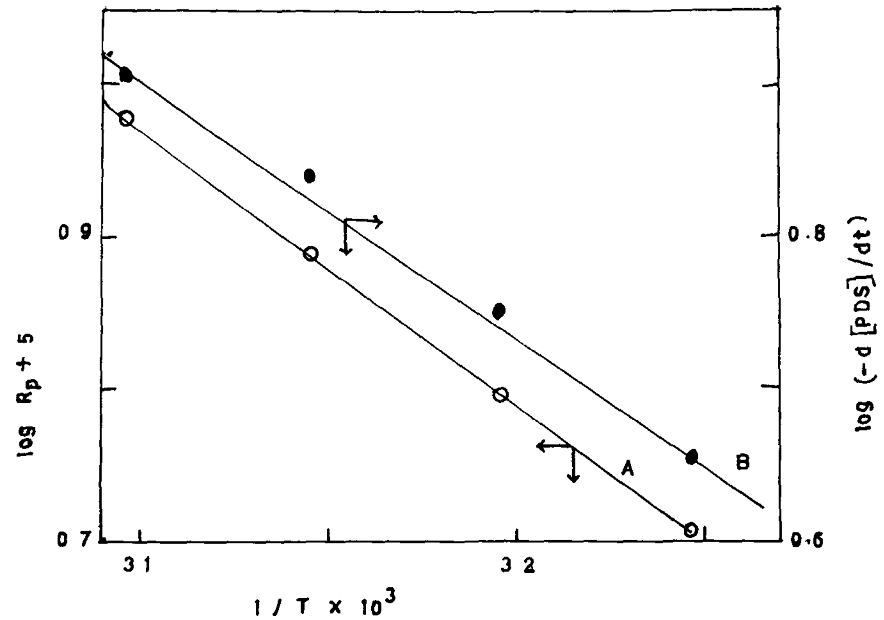

Fig. 5. Arrhenius plot for acrylamide polymerization and disappearance of PDS in the presence of ultrasound of frequency 1 MHz: $[M] = 0.4\ \mathrm{mol\ l^{-1}}$; $[PDS] = 8.32 \times 10^{-3}\ \mathrm{mol\ l^{-1}}$.

initiation observed in the presence of ultrasound involves abstraction or is a reaction with primary radicals.

From the plot of $-\,d[PDS]/dt$ versus $1/T$ (Arrhenius plot, Fig. 5), E_a of the PDS initiated polymerization of acrylamide was calculated to be 40 kJ $\mathrm{mol^{-1}}$ which is lower than for the thermal decomposition [18,19] of PDS alone (130 kJ $\mathrm{mol^{-1}}$). The observed lower value for E_a also favours the proposed initiation step as in Eq. (1B).

Substituting the value of k_i in $(k_p/k_t^{1/2})k_i^{1/2}$, the values of $(k_p/k_t^{1/2})$ for acrylamide polymerization were evaluated and are presented in Table 1. The observed lower value for $(k_p/k_t^{1/2})$ in comparison to a previously obtained value [20] points out the possibility of reactions in addition to initiation, such as

$$M + PDS \rightarrow CH_2{=}CH\text{–}CHN^{\cdot}HSO_4 + {}^{\cdot}OH \qquad (7)$$

Remy et al. [21] have also reported the reaction between $SO_4^{\cdot -}$ and the amide group of the growing radical with the result of the formation of a branched structure for the polymer. These types of reactions may lower the efficiency of initiation and can decrease $(k_p/k_t^{1/2})$ which has been observed experimentally here.

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