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Effect of Phenols on the Acidic Permanganate/Thioglycerol Couple Initiated Polymerization of Methyl Acrylate

Rajani K. Samal[a]; S. C. Satrusallya[a]; G. Panda[b]
[a] Department of Chemistry, Ravenshaw College, Cuttack, India [b] Department of Chemistry, S.V.M. College, Cuttack, India

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Effect of Phenols on the Acidic Permanganate/Thioglycerol Couple Initiated Polymerization of Methyl Acrylate

RAJANI K. SAMAL* and S. C. SATRUSALLYA

Department of Chemistry
Ravenshaw College
Cuttack 753003, India

G. PANDA

Department of Chemistry
S.V.M. College
Jagatsinghpur, Cuttack, India

ABSTRACT

The effect of various phenols on the polymerization of methyl acrylate (MA) initiated by the acidic permanganate/thioglycerol redox couple has been studied in aqueous solution at 30°C. It was found that among the various phenols used, o-cresol, m-cresol, resorcinol, and quinol behave as very weak inhibitors but retard the reaction to a significant extent. Other phenols such as phenol, o-nitrophenol, p-nitrophenol, α-naththol, β-naphthol, catechol, and pyrogallol behave both as inhibitors, and retarders. The rate of this process is dependent upon the substituents in the phenol and often their position. However, it is noticed that all phenols, irrespective of their low or high values of transfer constants, retard

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*Author to whom all correspondence should be addressed.

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the rate of polymerization. The polymerization reaction has also been studied at 25-40°C in the absence of phenols by varying the concentrations of other components. The rate of polymerization increases with increases in the concentration of the monomer and reducing agent, and with the catalyst the rate increases in a low concentration range (≃ 0.005 M), but at higher concentrations (>0.005 M) the rate decreases. From the kinetic results a reaction scheme has been suggested.

INTRODUCTION

In common with the more familiar chain reactions, addition polyreactions are susceptible to catalysis and inhibition. The existence of an induction period was noted in many of the early investigations of vinyl polymerization [1]. The length of this induction period was somewhat ill-defined and it was suggested by researchers [2] that it is produced by impurities in the monomer. Similar observations were made by Foord [3] during the course of his investigation of the effect of organic compounds on the radical polymerization of styrene. From some 130 organic compounds tested as inhibitors, he found that quinones were more effective than other compounds. Since then interest has been paid by a number of workers [4-9] to the kinetics of vinyl polymerization in the presence of a multitude of quinones, with the objective of elucidating the mechanism of inhibition and retardation of polymerization. Caldwell et al. [10] investigated the mechanism of reaction between hydroquinone and polymethyl methacrylate free radicals by kinetic methods. Russell et al. [11] studied the effect of simple phenols on the polymerization of styrene initiated by AIBN. A review of the literature reveals that no attention seems to have been paid the study of the effect of phenols on redox initiated vinyl polymerization. Since phenols suffer oxidation easily in a reaction medium containing an oxidizing agent, they might exhibit an interesting phenomenon in redox initiated vinyl polymerization. We reported [12-21] on the kinetics of vinyl polymerization initiated by metal ions such as V(V), Cr(VI), Ce(IV), Mn(IV), and Mn(III) coupled with easily oxidizable mercaptans. In this laboratory there is a research program to study the effect of various phenols on vinyl polymerization initiated by a multitude of redox pairs comprising higher valency transition metal ions and easily oxidizable organic substrates. As a part of this research program, we here furnish a comparative report on the effect of phenols on the polymerization of methyl acrylate (MA) initiated by the acidic permanganate/thioglycerol redox couple and suggest the mechanism.

EXPERIMENTAL

Methyl acrylate (MA) from a local firm was first washed with 5% NaOH to remove the inhibitor, followed by distilled water to remove any trace of alkali, and finally dried over anhydrous calcium chloride. Potassium permanganate (BDH), sodium bisulfate (Riedel), and sulfuric acid (18 M AR) were used. Thioglycerol was distilled under reduced pressure and the middle fraction was collected. All other reagents were of BDH quality.

Water used for preparing solutions was distilled over alkaline permanganate and deionized by passage through Biodominrolit resin (Permutit Co., United Kingdom).

Nitrogen used for deaeration of the reaction mixture was purified by passage through Fieser's solution, saturated lead acetate, and finally distilled water. The reaction mixture containing all components except $KMnO_4$ solution were deaerated by passing oxygen-free nitrogen for 30 min and thermostated at the desired temperature. The required amount of $KMnO_4$ solution was added to the reaction mixture after passage of nitrogen through it. At desired time intervals the reactions were arrested and the reaction vessels were then kept in an ice bath to stop any further reaction. The precipitated polymer was filtered and dried to constant weight at 70°C. The rates of polymerization were obtained gravimetrically and the conversion percentages were calculated as reported earlier [20].

The molecular weights of the purified polymers were determined viscometrically by using the appropriate Mark-Houwink relationship. The viscosities of the polymer solutions (0.1%) were determined in an Ubbelohde-type suspended level dilution viscometer in acetone at 30°C using the relationship

$$[\eta] = 28.2 \times 10^{-3}\ \overline{M}_w^{\ 0.52}$$

RESULT AND DISCUSSION

Methyl acrylate (MA) was polymerized in aqueous sulfuric acid at 25-40°C in the presence of the acidic permanganate/thioglyceril redox couple. Figure 1 shows a typical set of conversion curves at 30°C for various thioglycerol (TG) concentrations (0.25×10^{-3} to 3×10^{-3} M) and at a fixed concentration of Mn(IV) (2×10^{-2} M). From these curves it is clear that the initial rate as well as the maximum conversion increases on increasing the concentration of TG up to 2×10^{-3} M, beyond which the rate decreases. This might be due to 1) an increase in the rate of oxidation of TG with respect to the rate of initiation and 2) the generation of an excess of primary radicals, which under the existing experimental conditions cause the premature termination of the growing polymer chains. We made similar observations in the case of Cr(VI)/thiourea initiated polymerization of acrylonitrile [12] and Mn(IV)/thioacetamide initiated polymerization of acrylonitrile [20].

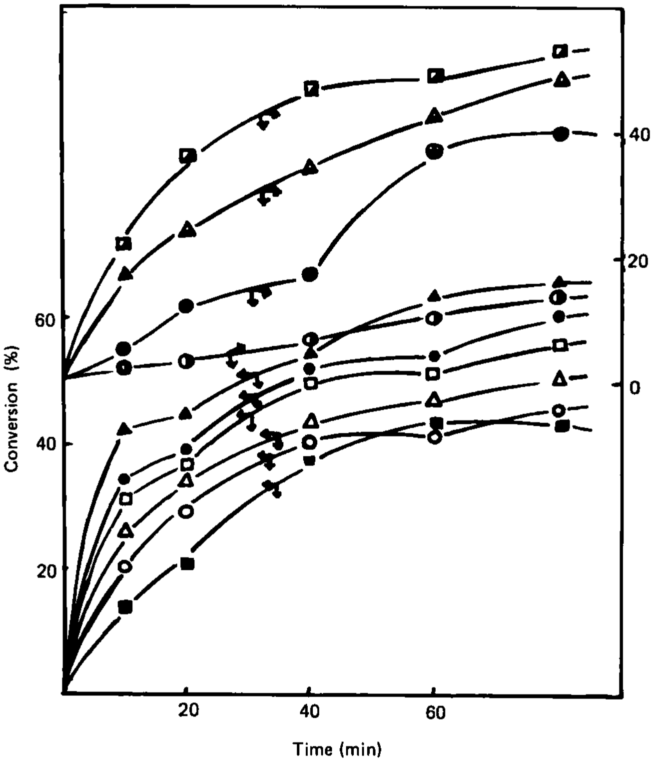


FIG. 1. Conversion percentage versus time: effect of activator concentration: [Mn(IV)] = 2 × 10^{-2} M, [H^+] = 0.45 M, [MA] = 0.11093 M, 30°C: [TG] = 0.25 × 10^{-3} M (○), 0.5 × 10^{-2} M, (△), 1 × 10^{-3} M (□), 1.5 × 10^{-3} M (●), 2 × 10^{-3} M (▲), 3 × 10^{-3} M (■). Conversion percentage versus time: effect of acid concentration: [Mn(IV)] = 1 × 10^{-2} M, [TG] = 2 × 10^{-3} M, [MA] = 0.1193 M, 30°C: [H^+] = 0.03 M (⊕), 0.075 M (▲), 0.15 M (◪), 0.6 M (◑).

Rate of Polymerization (R_p)

The rates of polymerization (R_p) increased regularly on increasing the concentration of the monomer (0.0554-0.3327 M). R_p also increased with an increase of temperature from 25 to 30°C, beyond which the rate decreased. Plots of log R_p vs log [MA] were linear at all temperatures

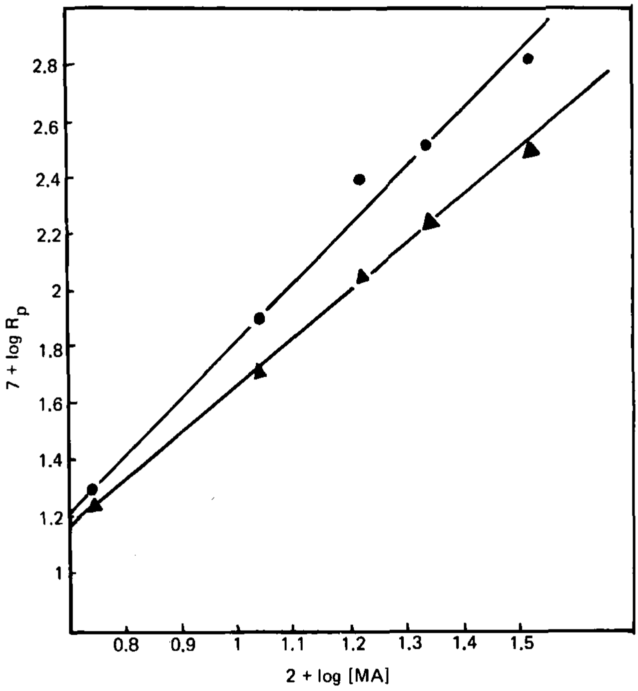


FIG. 2. Plots of (2 + log [MA]) vs (7 + log R_p): [Mn(IV)] = 1 × 10^{-2} M, [H^+] = 0.15 M, [TG] = 2 × 10^{-3} M. Temperature: 25°C (●), 40°C (▲).

(Fig. 2). At temperatures below 35°C the slope of the logarithm plots was 2, indicating a second-order dependence of the rate on monomer, but above 35°C the slope of the logarithm plots was 1.6 (≃ 1.5) indicating that at higher temperatures the rate with respect to the monomer was very close to 3/2.

Further, R_p also increased on increasing the concentration of the catalyst up to 0.1 to 0.9 × 10^{-2} M, beyond which the rate decreased. This might be due to premature linear termination of the growing polymer chains. The termination of the polymer chains by metal ions at higher concentrations is well recognized [22, 23]. A plot of log R_p vs log [Mn(IV)] at 25°C is shown in Fig. 3. In the temperature range of 20 to 30°C the slope of the plot is 0.33.

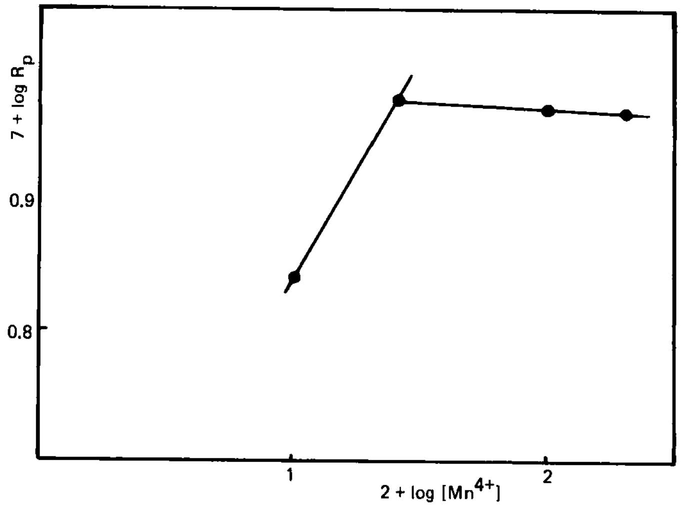


FIG. 3. Plot of (4 + log [Mn(IV)] vs (7 + log R_p): $[H^+]$ = 0.15 M, [TG] = 2 × 10^{-3} M, [MA] = 0.11093 M, 25°C.

Effect of Acid Concentration

The initial rate as well as the maximum conversion increased with an increase in the concentration of the acid (0.03-0.15 M). Beyond this concentration the rate decreased (Fig. 1). The most probable explanation of this phenomenon is that, under an optimum concentration of H^+ ions, $KMnO_4$ is slowly reduced to MnO_2 which interacts with the activator (TG) to produce the initiating radicals. When the concentration of H^+ ions is too high, Mn^{7+} ions are rapidly reduced to Mn^{2+} ions, as a result of which the optimum concentration of MnO_2 is not maintained. Also, the rate of oxidation of the activator to the products by acidified $KMnO_4$ becomes very fast, which reduces the rate of initiation.

Effect of Catalyst Concentration

The conversion curves at 30°C for various concentrations of the catalyst ($KMnO_4$) are computed in Fig. 4. From the curves it is noted that the conversion percentage increases with an increase in the concentration of the catalyst within 0.001-0.005 M and then decreases for higher concentrations. This is due to the premature linear termination of the polymer chains, as described in the case of R_p.

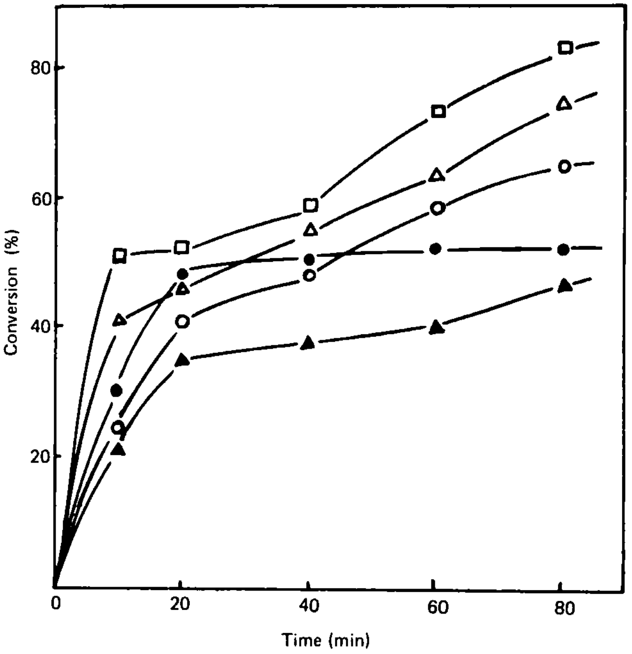


FIG. 4. Conversion percentage versus time: effect of catalyst concentration: [H] = 0.45 M, [TG] = 2 × 10^{-3} M, [MA] = 0.11093 M, 30°C. [Mn(IV)] = 0.001 M (○), 0.0025 M (△), 0.005 M (□), 0.01 M (●), 0.025 M (▲).

Effect of Phenols

The conversion percentages for various phenols at 30°C are computed in Fig. 5. The values of the conversion percentage at various times along with the respective induction periods are noted in Table 1. From these data it is clear that the polymerization rate is retarded in the presence of all the phenols, and moderate inhibition is marked in the case of phenol, o-nitriphenol, p-nitrophenol, catechol, pyrogallol, α-naphthol, and β-naphthol. However, phenols such as o-cresol, m-cresol, resorcinol, and quinol, although retarding the rate of polymerization, show very little if any inhibition. The larger rate of inhibition of o-nitriphenol and p-nitrophenol is quite reasonable in the sense that in these compounds both the phenolic OH group and the nitro group interfere with the growing polymer radicals as well as with the monomer molecules, as a result of which there is a long induction period

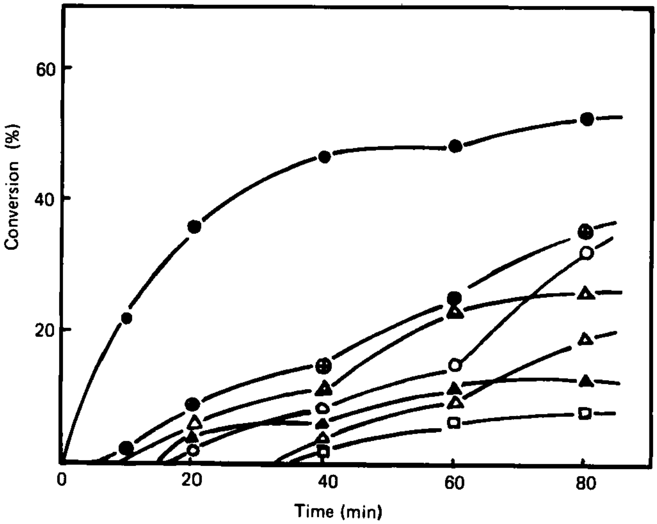


FIG. 5. Variation of conversion percentage with time: effect of various phenols: [Mn(IV)] = 0.01 M, [H^+] = 0.15 M, [TG] = 0.002 M, [phenol] = 0.5×10^{-4} M, 30°C. Control (●), phenol (○), p-nitrophenol (△), α-naphthol (□), β-naphthol (▲), quinol (▲), resorcinol (⊕).

and retardation in the rate. Similar observations were made by Price [24] in the case of quinones and by Azori et al. [25] in the study of the kinetics of styrene polymerization in the presence of aromatic nitro compounds using AIBN as initiator. Pyrogallol, catechol, and α-naphthol show greater retardation than phenol, and this may be attributed to their higher transfer constants (the transfer constant C of pyrogallol, catechol, α-naphthol, and phenol are 195×10^{-2}, 26.7×10^{-2}, 6.7×10^{-2}, and 0.14×10^{-2}, respectively). Significant retardation in the rate is also noticed with o-cresol, m-cresol, quinol, and resorcinol, even though they have low transfer constant values. From this we have come to the conclusion that, in our present investigation, all phenols, irrespective of their low or high transfer constant values, retard the rate of polymerization. Russell et al. [11], in their study of the effect of phenols on AIBN-initiated polymerization of styrene, observed that phenols with transfer constants lower than 8×10^{-3} behave as weaker retarding agents, but phenols with transfer constant greater than 8×10^{-3} exhibit significant retardation. The phenomenon observed in our case might be attributed to the simultaneous oxidation of the phenolics by Mn(IV) in the polymerization medium, for the differences in their rate of oxidation causes differences in their retarding ability. This

TABLE 1. Variation of Conversion Percentage with Time: Effect of Various Phenols ([Mn(IV)] = 0.01 M, $[H^+]$ = 0.15 M, [TG] = 0.002 M, [MA] = 0.11039 M, [phenol] = 0.5 × 10^{-4} M, 30°C)

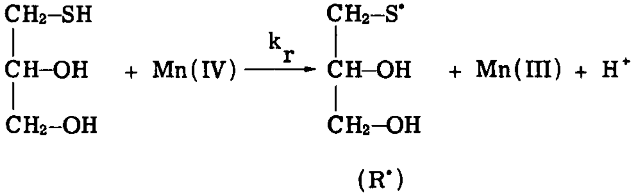
Phenol	Induction period (min)	Conversion percentage (min)				
		10	20	40	60	80
Control	1	22.978	36.035	47.002	49.48	53.791
Phenol	16	-	2.611	8.355	15.145	32.901
o-Nitrophenol	30	-	-	5.016	10.122	21.523
p-Nitrophenol	33	-	-	4.176	9.92	19.84
o-Cresol	6	1.5066	2.088	10.234	11.698	25.59
m-Cresol	4	2.080	7.756	12.011	17.234	25.06
Quinol	9	1.566	6.6112	11.091	24.54	26.11
Resorcinol	5	2.601	9.4	15.566	25.85	36.55
α-Naphthol	35	-	-	2.612	6.789	8.78
β-Naphthol	15	-	3.1334	6.1334	10.847	12.967
Catechol	25	-	-	4.912	9.912	16.005
Pyrogallol	28	-	-	3.104	8.076	13.967

seems to be true since the behavior of phenols changes when the acidic permanganate/thioglycerol redox couple is replaced by a nonoxidant like AIBN, as has been observed by Russell et al.

Reaction Mechanism and Rate Law

The polymerization of methyl acrylate (MA) in aqueous media initiated by acidic permanganate/thioglycerol shows features characteristic of heterogeneous polymerization. The reaction mixture becomes heterogeneous as soon as polymerization starts due to the insolubility of the polymer (PMA) in the aqueous phase.

From the kinetic results a reaction scheme has been proposed. It involves initiation by organic free radicals produced by the interaction of Mn(IV) with thioglycerol (TG) and termination by a linear path at low temperatures, mutual combination at high temperatures, and by added phenols.



$$\begin{array}{l}CH_2\text{–}SH\\ |\\ CH\text{–}OH\\ |\\ CH_2\text{–}OH\end{array} + Mn(IV) \xrightarrow{k_r} \underset{(R^{\bullet})}{\begin{array}{l}CH_2\text{–}S^{\bullet}\\ |\\ CH\text{–}OH\\ |\\ CH_2\text{–}OH\end{array}} + Mn(III) + H^+ \qquad (1)$$

$$R^{\bullet} + Mn(IV) \xrightarrow{k_0} \text{products} + Mn(II) \qquad (2)$$

$$Z + Mn(IV) \xrightarrow{k_0'} \text{oxidation product} + Mn(II) \quad (Z = \text{phenols}) \qquad (3)$$

Initiation:

$$R^{\bullet} + M \xrightarrow{k_i} R\text{–}M_1^{\bullet} \qquad (4)$$

Propagation:

$$\begin{array}{l} R\text{–}M_1^{\bullet} + M \xrightarrow{k_p} R\text{–}M_2^{\bullet} \\ \vdots \\ R\text{–}M_{n-1}^{\bullet} + M \longrightarrow R\text{–}M_n^{\bullet} \end{array} \qquad (5)$$

Termination:

Linear:

$$R\text{–}M_n^{\bullet} + Mn(III) \xrightarrow{k_t} \text{polymer} + Mn(II) + H^+ \qquad (6a)$$

Mutual:

$$R\text{–}M_n^{\bullet} + R\text{–}M_m^{\bullet} \xrightarrow{k_{t_1}} \text{polymer} \qquad (6b)$$

By phenols:

The growing polymer radicals may suffer premature termination in the presence of phenols which behave as both retarders and inhibitors:

$$R\text{–}M_n^{\bullet} + Z \xrightarrow{k_{t_2}} \text{polymer} + Z^{\bullet} \qquad (6c)$$

It is assumed that the radical $Z^{\bullet}$ does not initiate polymerization, and that the reaction is terminated without regenerating Z.

Applying the steady-state principle to the primary radical and to the growing polymer chains, and taking the radical reactivity as independent of radical size, for all types of terminations we obtain

$$R_p = \frac{k_r k_i k_p [Mn(IV)] [TG] [M]^2}{k_t [Mn(III)] (k_i [M] + k_0 [Mn(IV)])} \tag{7}$$

Substitution for [Mn(III)] in (7) yields

$$R_p = \frac{k_r k_i k_p [Mn(IV)] [TG] [M]^2}{k_t (k_0 [Mn(IV)] + k_i [M])^2} \tag{8}$$

If $k_0[Mn(IV)] \gg k_i[M]$

$$R_p = \frac{k_r k_i k_p [TG] [M]^2}{k_t k_0^2 [Mn(IV)]} \tag{9}$$

For mutual combination:

$$R_p = \frac{k_p k_i^{1/2} k_r^{1/2} [Mn(IV)]^{1/2} [TG]^{1/2} [M]^{3/2}}{(k_{t_1})^{1/2} (k_i [M] + k_0 [Mn(IV)])^{1/2}} \tag{10}$$

If $k_0[Mn(IV)] \gg k_i[M]$

$$R_p = \left(\frac{k_i k_r}{k_{t_1} k_0} \right)^{1/2} k_p [TG]^{1/2} [M]^{3/2} \tag{11}$$

Relations (9) and (11) hold good at 25 and 40°C, respectively (Fig. 2).

Termination of phenols:

$$R_p = \frac{k_r k_i k_p [TG] [M]^2}{k_0 k_{t_2} [Z]} \tag{12}$$

According to Eq. (12), R_p is inversely proportional to the concentration of added phenols, which is found to be true.

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