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Polymerization of Acrylonitrile Initiated by $K_2S_2O_8$ -Co(II) and $K_2S_2O_8$ -Mn(II) Redox Systems

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ABSTRACT

The kinetics of the aqueous polymerization of acrylonitrile initiated by the peroxydisulfate-Co(II) and peroxydisulfate-Mn(II) redox systems were investigated between 40 and 60°C. The rates of polymerization were measured at various concentrations of oxidant, activator, and monomer. From the results it was concluded that the polymerization reaction is initiated by an organic free radical arising from the peroxydisulfate-Co(II) and peroxydisulfate-Mn(II) redox systems and termination by the mutual type. On the basis of experimental observations of the dependence of the rate of polymerization R_p on various variables, a suitable kinetic scheme has been proposed.

INTRODUCTION

The use of peroxydisulfate ion as an oxidant for several classes of organic compounds and study of the kinetics of these processes have been carried out by different workers [1-4]. Work on the oxidation of a variety of organic and inorganic substrates by peroxydisulfate ion up to 1962 was reviewed by House [1] and Wilmarth and Halm [2]. In recent years the kinetics and mechanism of the peroxydisulfate oxida-

tion of organic compounds catalyzed by a number of metal ions, such as Ag(I) [4], Fe(II) [5], and Zn(II) [5], has attracted the attention of several groups of workers.

The polymerization of certain vinyl monomers initiated by peroxydisulfate was reported by Bacon [6] as early as 1946. Peroxydisulfate ion, coupled with monovalent silver ion, acts as a better initiator since Ag^{2+} produced during the process is a more powerful initiator than the peroxydisulfate ion alone. We have reported the kinetics and mechanism of the polymerization of acrylonitrile and methyl methacrylate initiated by peroxydisulfate catalyzed by metal ions [7, 8].

This communication reports the polymerization of acrylonitrile initiated by peroxydisulfate-Co(II) and peroxydisulfate-Mn(II) redox systems.

EXPERIMENTAL

All reagents used were of Analar grade. Acrylonitrile (American Cyanamide Co.) was purified by a standard method. Peroxydisulfate (PS) and ferrous sulfate were of BDH (Analar) grade. Pure distilled water redistilled over alkaline potassium permanganate and free of carbon dioxide was used throughout this investigation. The polymerization reaction was carried out according to our previous procedure [7, 8].

RESULTS AND DISCUSSION

Acrylonitrile was polymerized at 60°C in the presence of PS-Co(II) and PS-Mn(II) redox systems. Typical sets of time-conversion curves at different monomer (Fig. 1), metal ion (Fig. 2), and peroxydisulfate (Fig. 3) concentrations were drawn. The rate of polymerization increases linearly with time.

Dependence of Rate on Peroxydisulfate Concentration

The influence of [PS] on R_p was studied over a fivefold concentration range (1.25×10^{-3} to 6.25×10^{-3} M) in the case of the PS-Co(II) system and (2.5×10^{-3} to 12.5×10^{-3} M) in the case of the PS-Mn(II) system within the temperature range of 40 to 60°C. The plot of R_p versus [PS]^{1/2} (Fig. 4) is linear, indicating 0.5 order with respect to the oxidant concentration. Similar results have been reported by various workers [9-11]. This indicates that the termination process occurs by mutual collision of two active centers and that the steady-state approximation is well fulfilled.

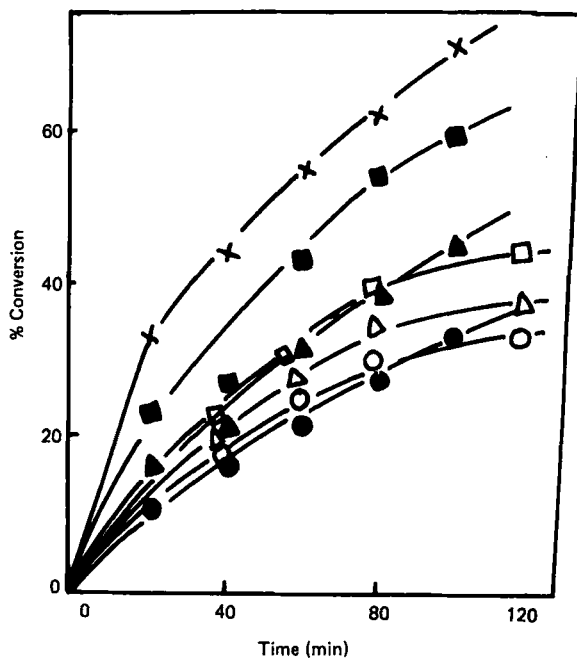


FIG. 1. Conversion-time curves. (a) $[PS] = 1 \times 10^{-2} \text{ M}$; $[Mn(II)] = 7.5 \times 10^{-3} \text{ M}$; $[H^+] = 3 \times 10^{-1} \text{ M}$; 60°C ; (\circ) $[AN] = 0.45 \text{ M}$; (Δ) $[AN] = 0.75 \text{ M}$; (\square) $[AN] = 1.05 \text{ M}$. (b) $[PS] = 5 \times 10^{-3} \text{ M}$; $[Co(II)] = 2.5 \times 10^{-3} \text{ M}$; $[H^+] = 3 \times 10^{-1} \text{ M}$; 60°C ; (\bullet) $[AN] = 0.3 \text{ M}$; (\blacktriangle) $[AN] = 0.6 \text{ M}$; (\blacksquare) $[AN] = 0.9 \text{ M}$; (\times) $[AN] = 1.2 \text{ M}$.

Dependence of Rate on Metal Ion Concentration

The effect of activator concentration on the rate of polymerization has been studied by changing the activator concentration from 1.25×10^{-3} to $6.75 \times 10^{-3} \text{ M}$ in the case of the PS-Co(II) redox system and 7.5×10^{-3} to $1.75 \times 10^{-3} \text{ M}$ in the case of the PS-Mn(II) redox system. Within the temperature range of 45 to 60°C the rate of polymerization was found to be increased linearly with increasing metal ion concentration in both cases (Fig. 5). It has been observed that peroxydisulfate alone is not a very good initiator for vinyl polymerization since the induction period is very high, but when peroxydisulfate is coupled with some metal ions like Ag(I), Fe(II), Co(II), or Mn(II), it acts as a better initiator. The reason for this is that the metal ion facilitates the formation of $SO_4^{\cdot-}$:

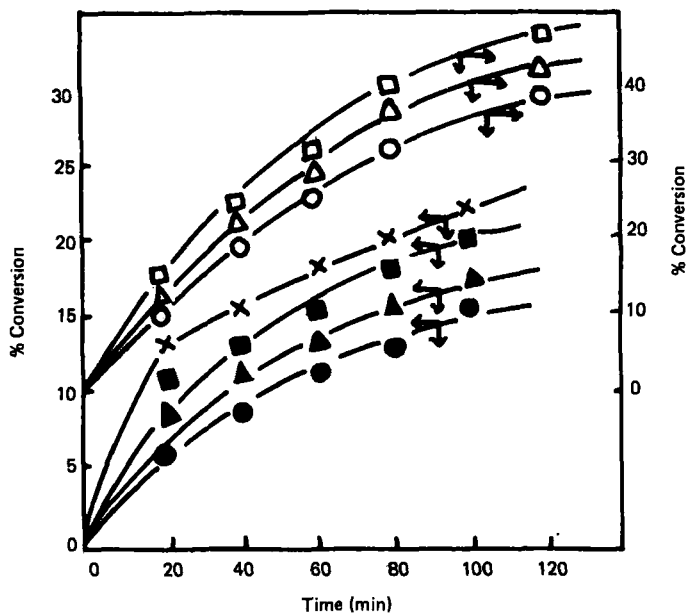


FIG. 2. Conversion-time curves. (a) $[PS] = 1 \times 10^{-2} \text{ M}$; $[AN] = 0.37 \text{ M}$; $[H^+] = 3 \times 10^{-1} \text{ M}$; 60°C ; (\circ) $[Mn(II)] = 2.5 \times 10^{-3} \text{ M}$; (Δ) $[Mn(II)] = 5 \times 10^{-3} \text{ M}$; (\square) $[Mn(II)] = 7.5 \times 10^{-3} \text{ M}$. (b) $[PS] = 5 \times 10^{-3} \text{ M}$; $[AN] = 0.37 \text{ M}$; $[H^+] = 3 \times 10^{-1} \text{ M}$; (\bullet) $[Co(II)] = 1.25 \times 10^{-3} \text{ M}$; (\blacktriangle) $[Co(II)] = 2.5 \times 10^{-3} \text{ M}$; (\blacksquare) $[Co(II)] = 3.75 \times 10^{-3} \text{ M}$; (\times) $[Co(II)] = 5 \times 10^{-3} \text{ M}$.



which initiates polymerization. Hence, with increasing Co(II) or Mn(II) concentration, a greater amount of $SO_4^{\cdot-}$ is formed, thereby increasing the rate of polymerization.

Dependence of Rate on Monomer Concentration

The rate of polymerization has been investigated by varying the monomer concentration from 0.30 to 1.5 M. The initial rate as well as the maximum conversion increases steadily with an increase of monomer concentration. The plot of R_p versus $[M]^{3/2}$ (Fig. 6) is linear, indicating a 1.5 order with respect to the monomer concentration.

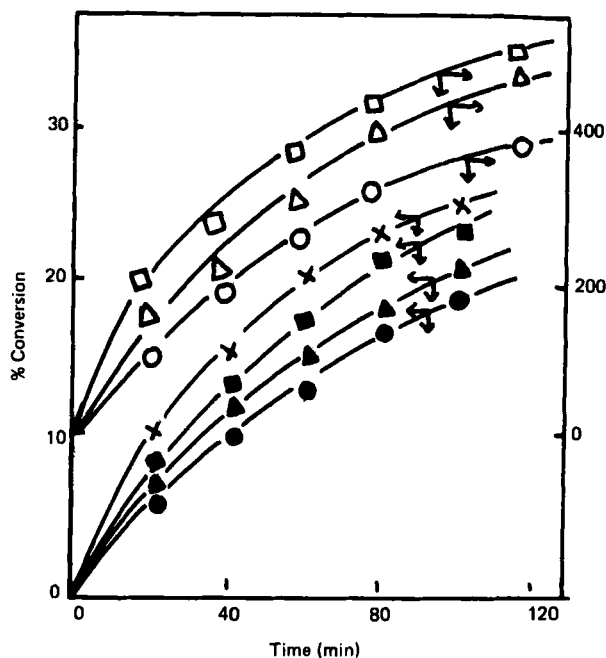


FIG. 3. Conversion-time curves. (a) $[\text{Mn(II)}] = 1 \times 10^{-2} \text{ M}$; $[\text{AN}] = 0.7 \text{ M}$; $[\text{H}^+] = 3 \times 10^{-1} \text{ M}$; 60°C ; (\circ) $[\text{PS}] = 2.5 \times 10^{-3} \text{ M}$; (Δ) $[\text{PS}] = 5 \times 10^{-3} \text{ M}$; (\square) $[\text{PS}] = 7.5 \times 10^{-3} \text{ M}$; (b) $[\text{Co(II)}] = 2.5 \times 10^{-3} \text{ M}$; $[\text{AN}] = 0.37 \text{ M}$; $[\text{H}^+] = 3 \times 10^{-1} \text{ M}$; 60°C ; (\bullet) $[\text{PS}] = 1.25 \times 10^{-3} \text{ M}$; (\blacktriangle) $[\text{PS}] = 2.5 \times 10^{-3} \text{ M}$; (\blacksquare) $[\text{PS}] = 3.75 \times 10^{-3} \text{ M}$; (\times) $[\text{PS}] = 5 \times 10^{-3} \text{ M}$.

Dependence of Rate on Micelles Concentration

The rate of polymerization has been investigated by varying the monomer, initiator, and metal ion concentrations in the presence of surfactants like sodium lauryl sulfate and cetyltrimethyl ammonium bromide. It is observed from the results that in the presence of surfactants, the value of R_p decreases. This might be due to the salt effect.

Dependence of Rate with Temperature

The reactions were carried out at various temperatures within the range of 40 to 60°C . The rate of polymerization increases with an in-

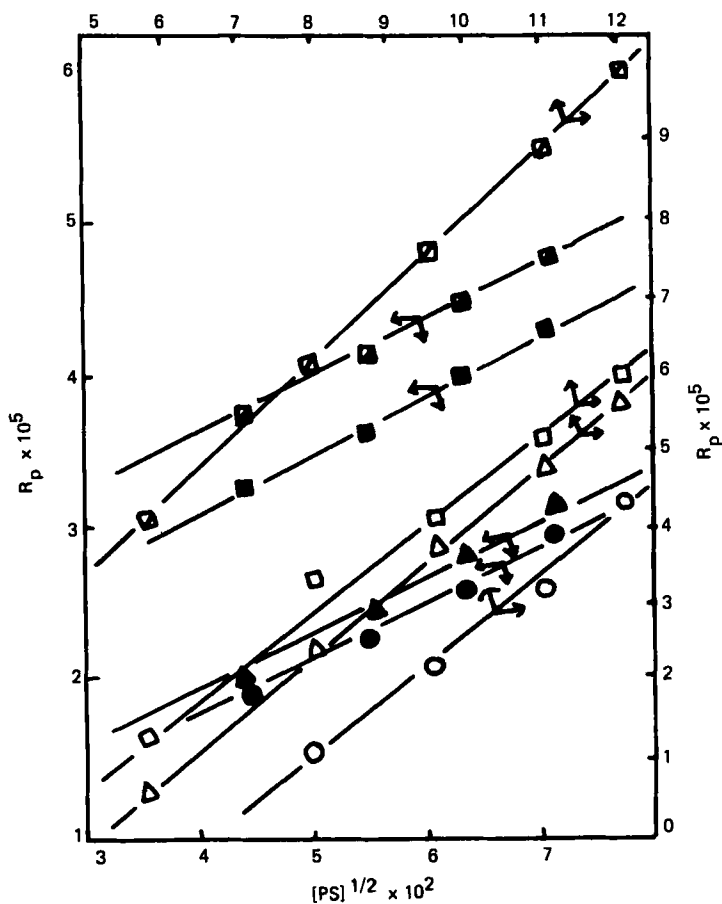


FIG. 4. Plot of R_p versus $[PS]^{1/2}$. (a) $[Mn(II)] = 7.5 \times 10^{-3} M$; $[AN] = 0.7 M$; $[H^+] = 3 \times 10^{-1} M$; 2 h; (○) 40°C; (△) 50°C; (◻) 55°C; (◻) 60°C. (b) $[Co(II)] = 2.5 \times 10^{-3} M$; $[AN] = 0.75 M$; $[H^+] = 3 \times 10^{-1} M$; 2 h; (●) 45°C; (▲) 50°C; (■) 55°C; (◻) 60°C.

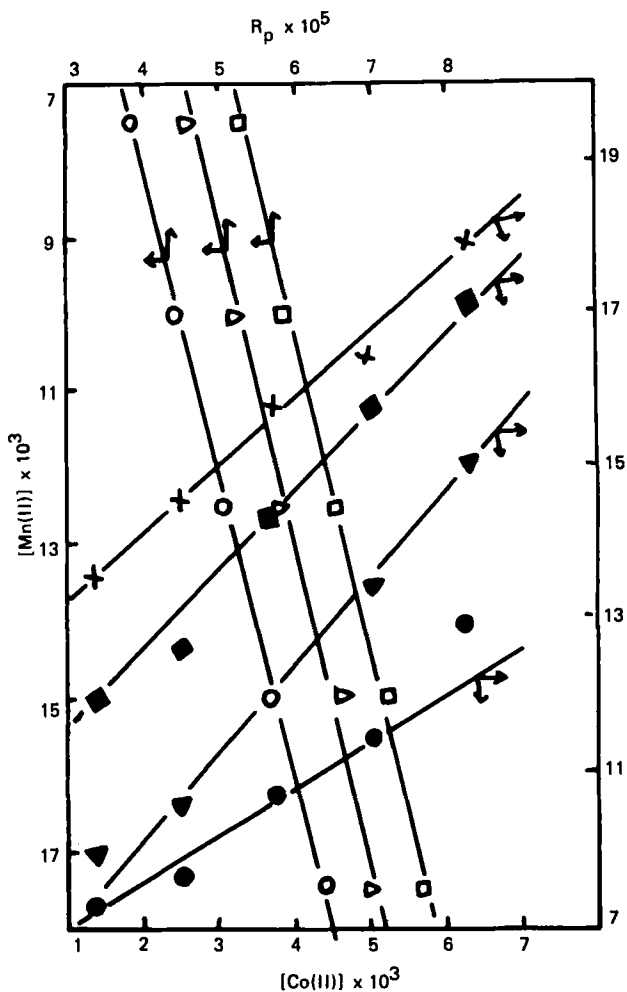


FIG. 5. (a) Plot of R_p versus $[Mn(II)]$: $[PS] = 1 \times 10^{-2} M$; $[AN] = 0.75 M$; $[H^+] = 3 \times 10^{-1} M$; 2 h; (o) $50^\circ C$; (Δ) $55^\circ C$; (\square) $60^\circ C$. (b) Plot of R_p versus $[Co(II)]$: $[PS] = 5 \times 10^{-3} M$; $[AN] = 0.37 M$; $[H^+] = 3 \times 10^{-1} M$. (o) $45^\circ C$; (Δ) $50^\circ C$; (\square) $55^\circ C$; (\times) $60^\circ C$.

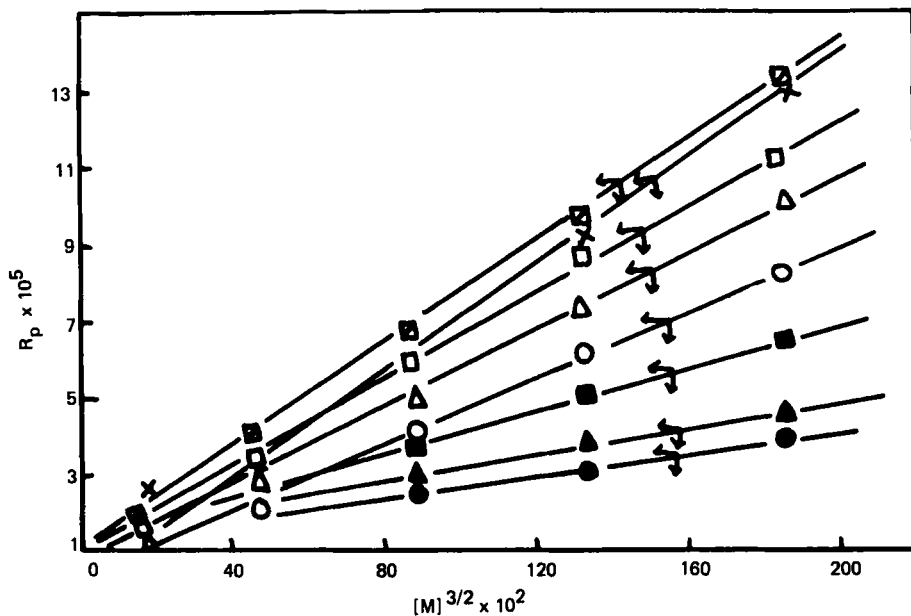


FIG. 6. Plot of R_p versus $[M]^{3/2}$. (a) $[PS] = 1 \times 10^{-2} \text{ M}$; $[Mn(II)] = 7.5 \times 10^{-3} \text{ M}$; $[H^+] = 3 \times 10^{-1} \text{ M}$; (\circ) 5°C ; (Δ) 50°C ; (\square) 55°C ; (\square) 60°C . (b) $[PS] = 5 \times 10^{-3} \text{ M}$; $[Co(II)] = 2.5 \times 10^{-3} \text{ M}$; $[H^+] = 3 \times 10^{-1} \text{ M}$; 2 h; (\bullet) 45°C ; (\blacktriangle) 50°C ; (\blacksquare) 55°C ; (\square) 60°C .

crease of temperature. From the slopes of the Arrhenius plot (Fig. 7) of $\log R_p$ versus $1/T$, the overall activation energies were computed to be 6.9 ± 0.5 and 5.2 ± 0.5 kcal/mol for PS-Co(II) and PS-Mn(II) redox systems, respectively.

Dependence of rate on Inhibitor Concentration

In 1925 Ostromyslensky [12] observed that the polymerization of styrene is inhibited by hydroquinone and aromatic nitro compounds. The effect of these compounds on the rate of polymerization was investigated more extensively by Foord [13] and later by Schulz [14]. It was stated that the retarding effect is enhanced by increasing the number of nitro groups. Various inhibition mechanisms have been suggested by Tüddös and co-workers [15, 16].

In the present investigation the inhibition of polymerization initiated by peroxydisulfate metal ion systems has been examined by using

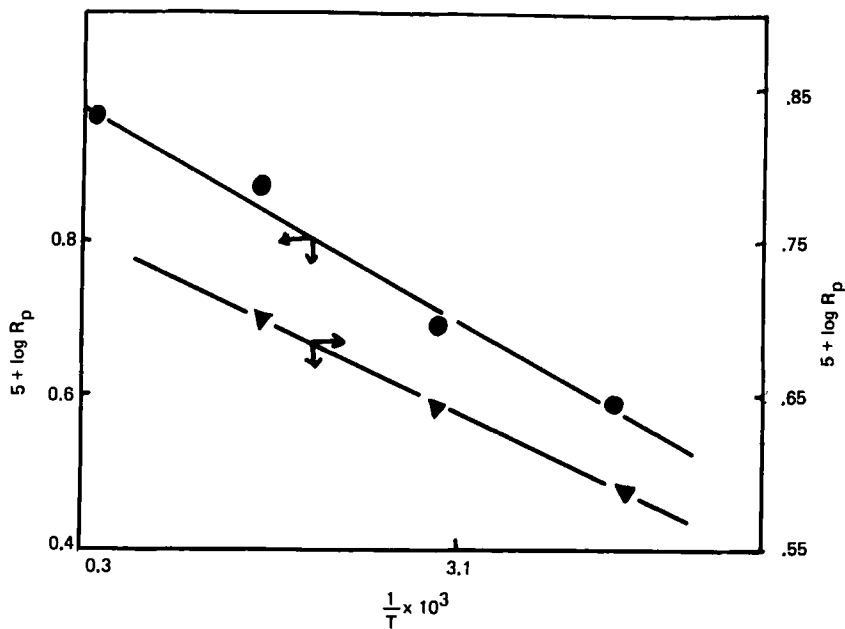


FIG. 7. Arrhenius plot of $\log R_p$ versus $1/T$: (●) PS-Mn(II) system; (▲) PS-Co(II) system.

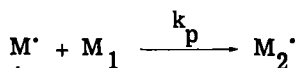
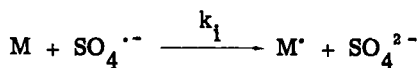
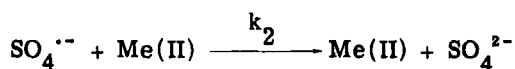
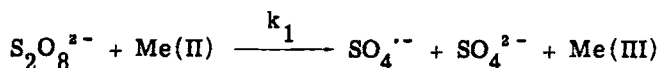
picryl chloride as the potential inhibitor. The rate of polymerization dramatically decreases with an increase in the concentration of the inhibitors.

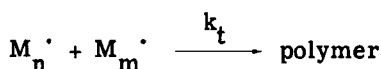
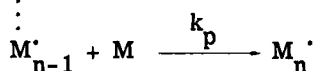
Dependence of Solvent on the Rate of Polymerization

Solvent plays an important role on the rate of polymerization. The rate or reaction was studied using a number of polar, dipolar, aprotic, and nonpolar solvents. The rate of reaction follows the order: methanol > dioxane > acetic acid > acetone > carbon tetrachloride.

MECHANISM

The dependence of the rate of polymerization on initiator, activator, and monomer concentration could be expressed by the following mechanism:



$$\vdots$$


Assuming the steady-state principle and considering that initiation is by $SO_4^{\cdot-}$ and termination is by the mutual type, the rate of polymerization R_p was computed to be

$$R_p = k_p \left[\frac{k_i}{k_t} \left(\frac{k_i [S_2O_8^{2-}] [Me(II)]}{k_i [M] + k_1 [Me(II)]} \right) \right]^{1/2} \times [M]^{3/2}$$

If $k_1 \gg k_i$,

$$R_p = k_p \left(\frac{k_i}{k_t} \right)^{1/2} [S_2O_8^{2-}]^{1/2} [M]^{3/2}$$

The above rate expression was satisfied by plots of R_p versus $[S_2O_8^{2-}]^{1/2}$ (Fig. 4) and R_p versus $[M]^{3/2}$, which are found to be linear (Fig. 6).

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