

Efficient and Novel Method for Surface Oxidation of Polypropylene in the Solid Phase Using Microwave Irradiation

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ABSTRACT: The oxidation of polypropylene in the solid phase in the presence of potassium permanganate was carried out using microwave irradiation. The oxidation was achieved at time intervals of 20, 40, 60, and 90 s. According to the data available from FTIR spectroscopy, the vinylic and carbonyl groups are observed on the polymer surface. It is noteworthy that by using this method of oxidation we have saved energy and time and also less pollution has been entered into the environment by minimum oxidant consumption with maximum efficiency. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1317–1323, 2001

Key words: polypropylene; microwave oven; surface oxidation; potassium permanganate; solid-state reaction

INTRODUCTION

The oxidation of polyolefins may be triggered by a catalyst, heat, light, or mechanical action, or high-energy radiation.^{1–10} The understanding of these oxidation reactions is important, both in the development of stabilizers to protect such oxidative degradation and in the use of selective degradation of low-cost polyolefins for specific applications. The most important properties such as color, tensile strength, and elongation in polyolefins are unaffected by surface-oxidation reactions. The presence of polar groups on the surface of a

polymer affects the adhesion and the compatibility of the polymer surface with polar materials like colorants and antioxidants.

However, oxidation of solid polymers is appreciably more complex than are the well-established oxidation mechanisms for liquid hydrocarbons. This complexity stems from restricted mobility effects in the solid phase.

In this article, we report a new and highly effective method for the oxidation of polypropylene (PP) under solid-state and microwave irradiation conditions. The major advantages of this technique are its simplicity, minimum reaction time, and energy consumption during the oxidation processes.

EXPERIMENTAL

Materials and Equipment

PP powder was obtained from Bandar-Imam Petrochemical Co. Bandar-Imam (I. R. Iran). Potas-

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sium permanganate was analytical grade and supplied by Hopkins & Williams (USA). FTIR spectra were recorded on a BOMEM–Hartmann & Broun–MB Series (England) spectrophotometer. The spectra of solids were carried out using KBr pellets. Thermal gravimetric analysis (TGA) data for the polymers were taken on a Stanton-650 TGA (England) under a N_2 atmosphere at a rate of $10^\circ C/min$. The microwave apparatus used here was a Samsung domestic microwave oven (2450 MHz, 900 W; South Korea).

Method

Oxidation of PP with $KMnO_4$ Without and With Microwave Irradiation (Experiment A)

PP powder, 1.0 g, and potassium permanganate, 1.3 g [(3:1 molar ratio of the repeating unit (RU) of PP to $KMnO_4$)], were ground finely in a mortar using a pestle. Sampling was performed, which exhibits the progress of the reaction with no microwave irradiation and under solid-phase conditions. The remainder was placed in the microwave oven and irradiated for 20 s. Then, it was washed with an excess amount of distilled water. For removal of MnO_2 adsorbed on the surface of the oxidized powders, it was washed with an aqueous solution of 20% H_2SO_4 and finally with distilled water until the pH of the filtrate reached 7.0. The powders were dried under reduced pressure at room temperature. Three other samples were prepared in a similar way to the above procedure using 40-, 60-, and 90-s time-interval irradiation. Here, all experiments were carried out at a constant microwave power (i.e., 900 W).

Oxidation of PP with $KMnO_4$ at Different Molar Ratios of PP/ $KMnO_4$ Under Microwave Irradiation (Experiment B)

According to the above procedure at 90-s microwave irradiation time, the PP/ $KMnO_4$ ratios were varied. So, similar experiments were carried out with 0.5 g PP powder and 0.33 g potassium permanganate (6:1 molar ratio). Other molar ratios were (I) 0.5 g PP powder and 0.19 g potassium permanganate (10:1 molar ratio), (II) 0.75 g PP powder and 0.19 g potassium permanganate (15:1 molar ratio), (III) 1.0 g PP powder and 0.19 g potassium permanganate (20:1 molar ratio), and (IV) 0.5 g PP powder and 0.038 g potassium permanganate (50:1 molar ratio). The workup procedure is similar to that pointed out in Experiment A.

Oxidation of PP with $KMnO_4$ Under Microwave Irradiation with Variation in Power of Microwave at Constant PP/ $KMnO_4$ Molar Ratio and Irradiation Time (Experiment C)

According to the procedure reported in Experiment A at 90-s microwave irradiation time, the microwave power was varied at a constant molar ratio of the RU of PP powder and potassium permanganate. So, three samples of 0.5 g PP powder and 0.65 g potassium permanganate (3:1 molar ratio) were ground finely in a mortar using a pestle and then were placed in the microwave oven. The first one was irradiated for 90 s at the power of 900 W. The second sample was irradiated for 90 s at the power of 450 W, and the third sample was irradiated for 90 s at the power of 90 W. The workup procedure is similar to that pointed out in Experiment A.

RESULTS AND DISCUSSION

Oxidation was performed according to the procedure represented in the Experimental section. After washing with distilled water, we could see the progress of the reaction. The powder becomes pale brown, which shows the absorption of MnO_2 produced during the oxidation reaction. Infrared spectroscopy is the basic and accurate technique for surface analysis.¹¹ In this manner, FTIR spectra of the oxidized PP after 90-s microwave irradiation (Experiment A), the original PP powder, and the microwave-irradiated PP for 90 s in the absence of an oxidizing agent are recorded comparably (Fig. 1). However, the presence of two extra peaks at 1590–1810 and 1590–1497 cm^{-1} in the oxidized PP after 90-s microwave irradiation (Experiment A) confirms the progress of the oxidation reaction. These two peaks do not exist in the two other samples and all other peaks are similarly repeated. Such information reveals that the oxidation reaction occurred only in the sample of PP under irradiation in the presence of potassium permanganate. According to the data available in the literature,¹² we could relate these two peaks to the formation of α,β -unsaturated carbonyl compounds. The peak in the region of 1590–1810 cm^{-1} is related to the C=O stretching band and the other peak at 1497–1590 cm^{-1} concerns the C=C stretching vibration. The C=C bending vibrations which are in the region of about 1300–1400 cm^{-1} are overlapped with the symmetrical

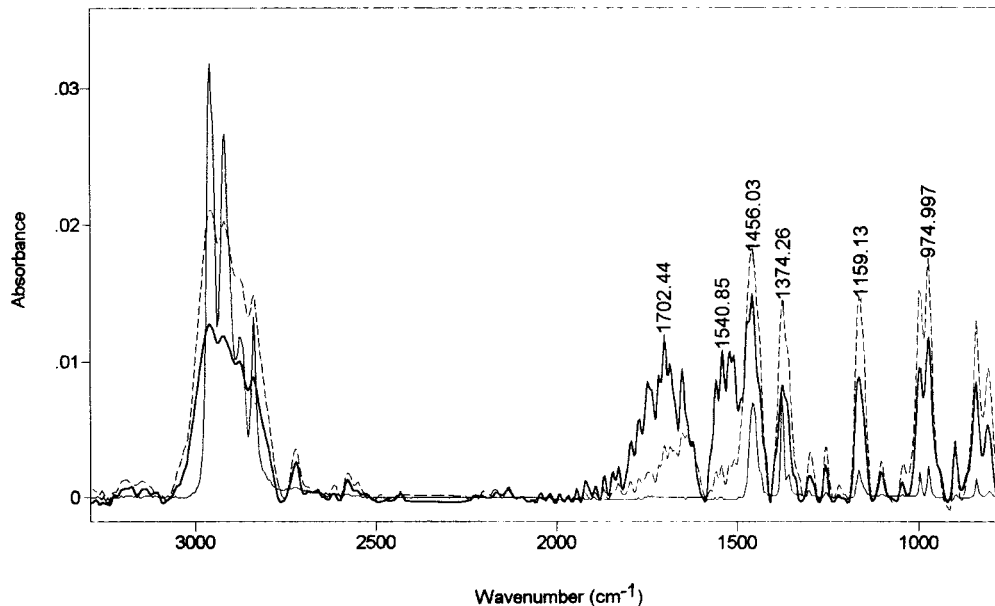


Figure 1 FTIR spectra of (—) original PP, (---) 90-s microwave-irradiated PP, and (— · —) oxidized PP after 90-s irradiation.

and asymmetrical bending vibrations of CH_3 in the PP at 1374 and 1456 cm^{-1} , respectively. So, we could conclude that the oxidation reaction proceeds through the formation of carbonyl and also alkene functional groups in which they are mainly in conjugation with each other.

In Figure 2, we investigated the effect of the duration and also the variation in the time of microwave irradiation at a constant molar ratio. It is notable that under solid-phase conditions (i.e., 0-s irradiation time) no considerable progress in the oxidation reaction was observed.

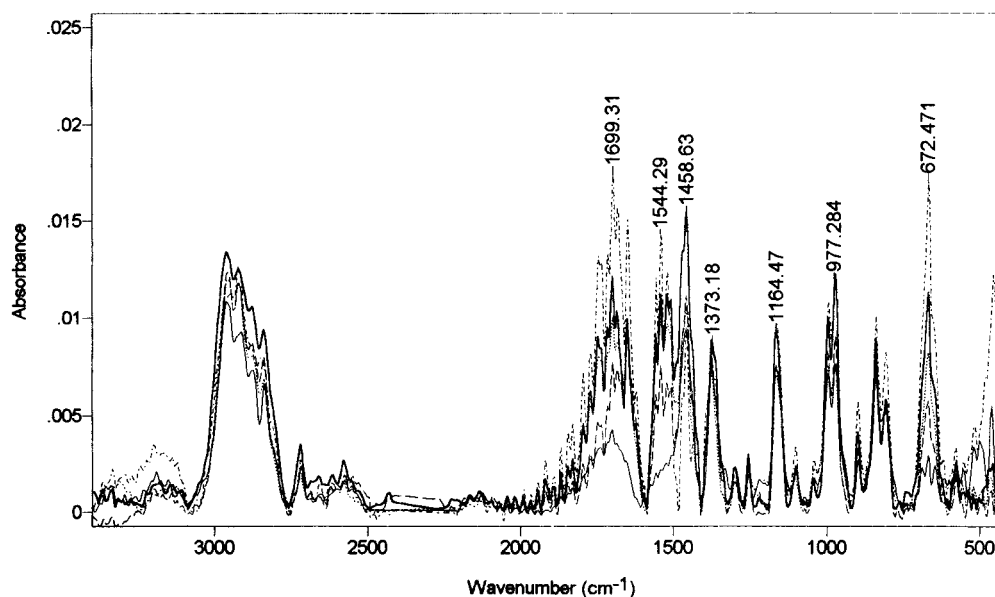


Figure 2 FTIR spectra of samples, (—) under solid-state condition after (---) 20-s, (····) 40-s, (— · —) 60-s, and (—) 90-s irradiation time.

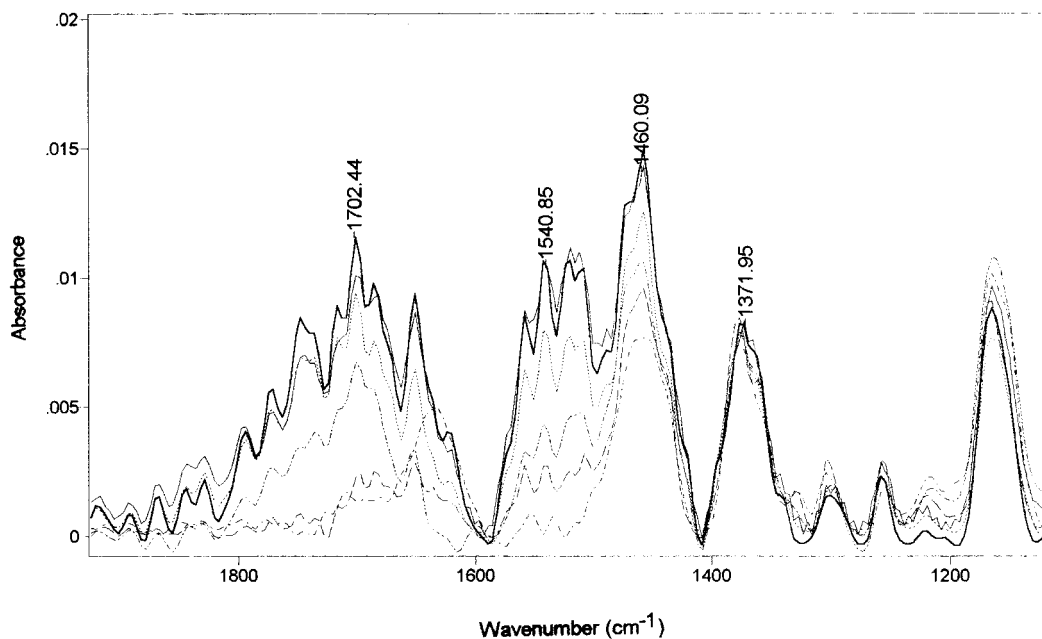


Figure 3 FTIR spectra of oxidized samples, in PP/KMnO₄ (—) 3:1, (· · · ·) 6:1, (—) 10:1, (· · · · · ·) 15:1, (- · - · -) 20:1, and (- - - -) 50:1 molar ratio.

But after only 20-s microwave irradiation, the two characteristic peaks (1590–1810 cm⁻¹ and 1497–1590 cm⁻¹) appeared. By increasing this irradiation time up to 90 s, the intensity of these two peaks did not increase much and more microwave irradiation time causes the melting and probably

the decomposition of the PP in the microwave oven. Therefore, this irradiation time (90 s) would be the upper limit time for this oxidation. Also, it should be noted that to compare the intensity of the peaks the characteristic peak of PP at 1373 cm⁻¹ for each spectra was equalized. To verify the

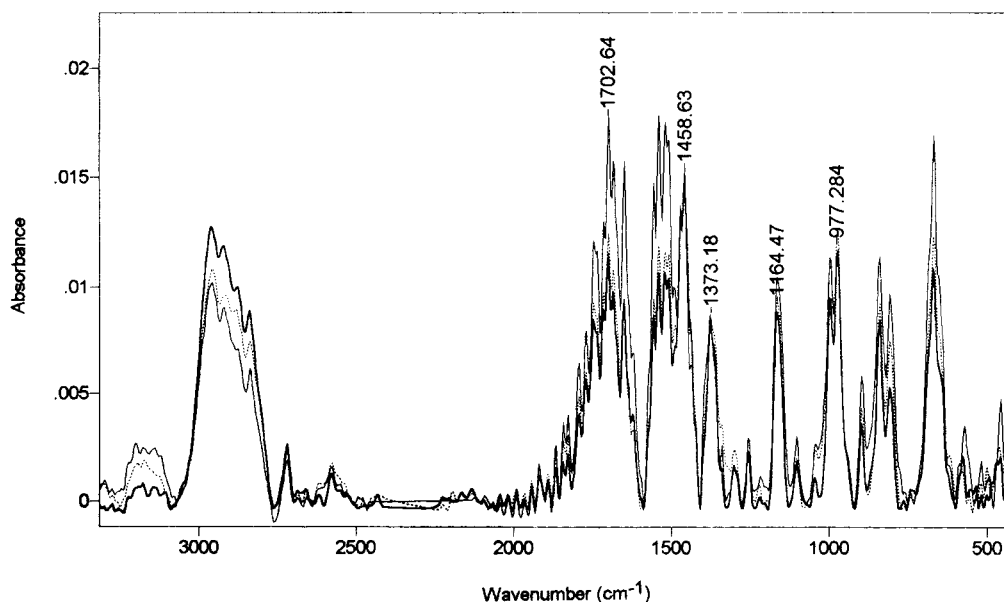


Figure 4 FTIR spectra of oxidized samples, at (—) 900-W, (· · · ·) 450-W, and (—) 90-W irradiation power.

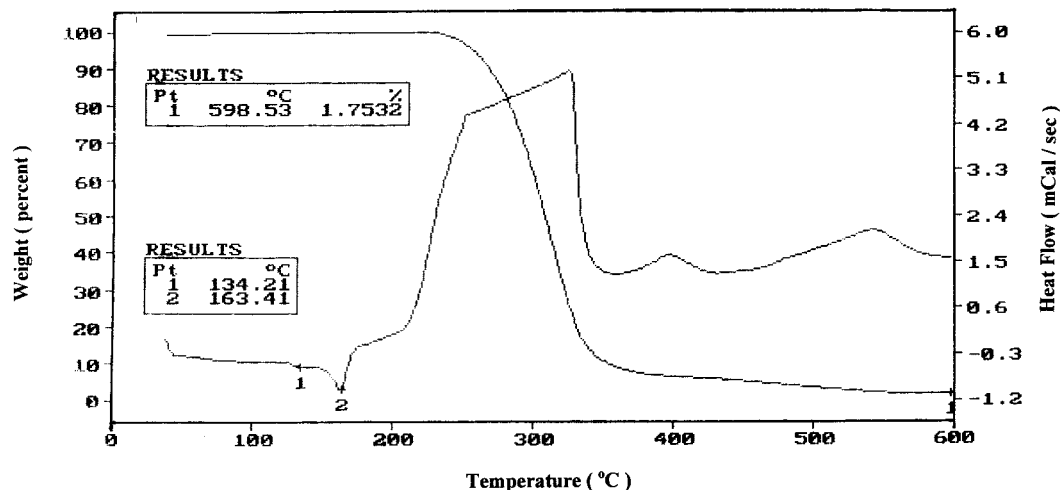


Figure 5 TGA and DTG thermograms for original PP.

effect of variation in the molar ratio of PP and KMnO_4 , we designed Experiment B. As shown in Figure 3 (expanded region), by increasing the molar ratio of the RU of PP to potassium permanganate from 3:1 to 6:1 and even to 10:1, no significant change was observed. But in increasing this ratio to 15:1, some decrease in the intensities of the two characteristic bands are observed. This decrease continues at a 20:1 molar ratio, and after reaching a 50:1 molar ratio, the oxidation reaction was stopped. Thus, these data show that we can decrease the molar ratio of an oxidant even to 10:1 without any disturbance in the oxidation process. Therefore, this is economically important in addition to environmental aspects because less

oxidant is being used and, as a result, less water-soluble pollutants are entered into our environment.

We also studied the effect of the variation in microwave power (Experiment C). Here, three input powers were considered, which are 900, 450, and 90 W at the same molar ratio of PP to KMnO_4 . As shown in Figure 4, after equalization of the peak at 1373 cm^{-1} , the functional group bands at $1590\text{--}1810\text{ cm}^{-1}$ and $1497\text{--}1590\text{ cm}^{-1}$ have the same intensities for both 900- and 450-W input power. But at 90-W input power, there is little increase in these two characteristics bands. This evidence reveals that we have similar results by spending less energy, that is, here we achieved

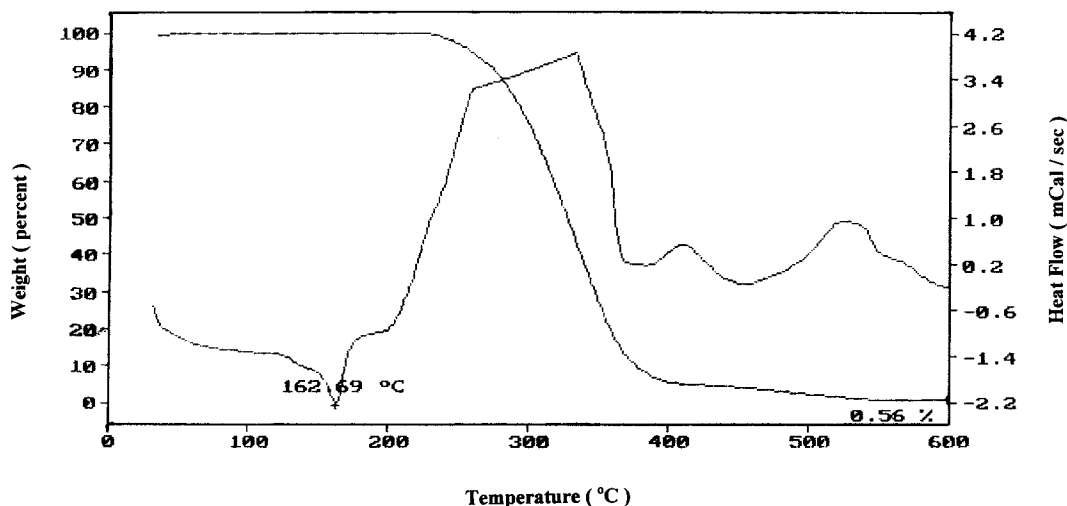
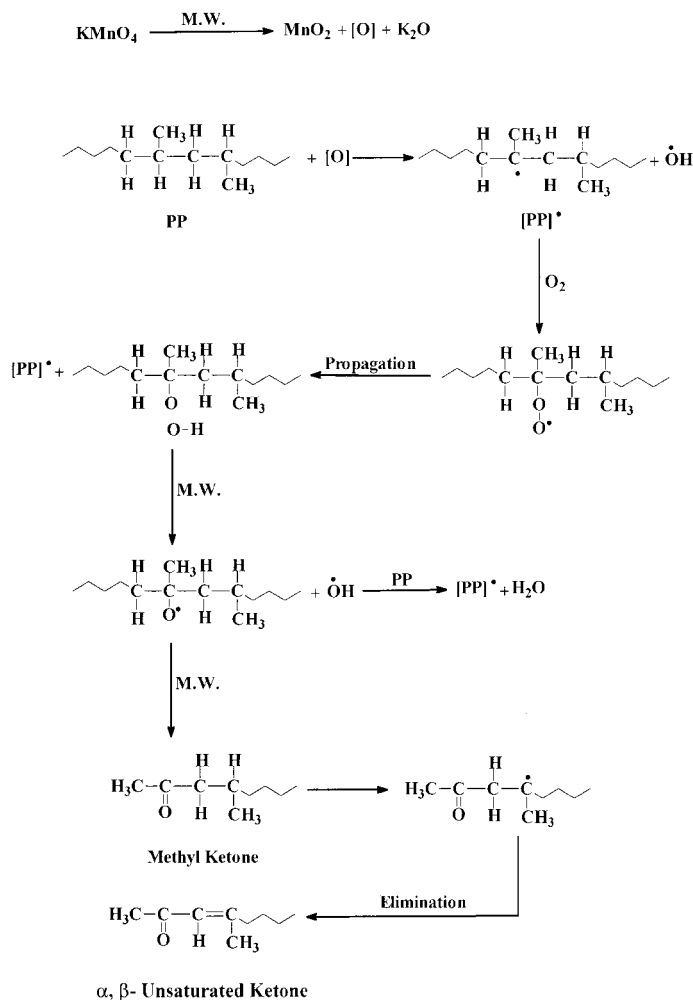


Figure 6 TGA and DTG thermograms for oxidized PP after 90-s irradiation and PP/KMnO_4 3:1 molar ratio.



Scheme 1

a method with a minimum consumption of energy. It is important to note that we selected the maximum PP/KMnO₄ (3:1) molar ratio and irradiation time (90 s) for the investigation of the effect of the variation in microwave power on the oxidation reaction. The reason for these selections is to give enough opportunity for probable side reactions during this process to occur.

Also, according to the data available from the TGA and DSC thermograms, the thermal properties of PP before any modification (Fig. 5) and after 90-s irradiation in the presence of potassium permanganate with a PP/KMnO₄ (3:1) molar ratio (Fig. 6) are identical. These results confirm that the surface modification occurred without any changes in the thermal properties of the polymer.

Mechanistical Studies

Several reports exist on the oxidation of PP conducive to the formation of carbonyl groups, but more detailed mechanistical studies were presented by Adams.¹⁰ The most probable mechanism according to the data obtained from FTIR spectroscopy is proposed in Scheme 1. In this proposed mechanism, atomic oxygen is generated from potassium permanganate and initiates the surface oxidation of PP by producing the tertiary radical. This radical will capture O₂ from the atmosphere and give the hydroperoxide derivative. Subsequently, decomposition of this hydroperoxide and chain scissoring result in the formation of carbonyl groups. Furthermore, elimination of hydrogen will furnish an α,β -unsaturated carbonyl compound.

CONCLUSIONS

We developed, for the first time, a new and facile method for the rapid surface oxidation of PP with potassium permanganate as a readily available and cheap oxidizing agent using a domestic microwave oven. The oxidation occurs under mild conditions and leads to the formation of vinylic and carbonyl functional groups. Since this oxidation is carried out under solvent-free conditions, the cost of the solvent has been eliminated. Therefore, we have achieved an efficient oxidation of PP in a simple way with an inexpensive and routine method with minimum time, energy consumption, and low cost. Furthermore, this oxidation does not effect the thermal properties of PP.

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