Synthesis of Crosslinked Superabsorbent Carboxymethyl Cellulose/Acrylamide Hydrogels Through Electron-Beam Irradiation

Sayeda M. Ibrahim, Kariman M. El Salmawi, A. H. Zahran

Department of Radiation Chemistry, National Center for Radiation Research and Technology, P.O. Box 29, Nasr City, Cairo, Egypt

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ABSTRACT: A study on the possibility of the preparation of superabsorbent hydrogels based on crosslinked carboxymethyl cellulose polymer and acrylamide monomer through electron-beam irradiation was carried out. The effects of the irradiation dose and polymer–monomer compositions on the crosslinking density were studied. The hydrophilic properties of the superabsorbent hydrogels were identified by the swelling percentage. The prepared hydrogels had higher swelling in distilled water than in salt solutions. Moreover, the hydrogels exhibited the highest swelling at pH 7. Also, increasing the temperature up to 50°C caused an increase in the swelling. The thermal properties of the hydrogels were characterized with thermogravimetric analysis. The use of the prepared superabsorbent hydrogels for the growth of rice was also investigated through the water-retention property. The water retention in the soil was enhanced with the hydrogels. Superabsorbent hydrogels based on carboxymethyl cellulose polymer and acrylamide monomer could be considered as water-managing materials for agriculture and horticulture in desert and drought-prone areas. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2003–2008, 2007

Key words: hydrogels; hydrophilic polymers; irradiation; swelling; water-soluble polymers

INTRODUCTION

The application of superabsorbents to agriculture is a growing field of interest. Superabsorbents have been reported as good soil-conditioning materials.[1–4] Hydrogels can be used as superabsorbents because of their excellent characteristics. These superabsorbents are widely used in many products, such as disposable diapers, feminine napkins, soil for agriculture and horticulture, gel actuators, water-blocking tapes, medicine for drug-delivery systems, and absorbent pads, for which water absorbency or water retention is important.[5–12]

Carboxymethyl cellulose (CMC) is an anionic and water-soluble natural polymer derivative that is widely used in detergents, in oil exploration, and in the food, paper, and textile industries because of its viscosity-increasing properties.[13] CMC, similar to other natural cellulosic polymers, is a degradable polymer under irradiation but can be crosslinked to form a hydrogel under suitable conditions, as reported by Liu and coworkers.[14,15]

Some workers have modified these superabsorbent copolymers (SAPs) to enhance their absorbency, gel strength, and absorption rate.[16–21] The influences of various reaction parameters on the water-absorption capacity of SAPs have been investigated by various workers.[22,23] The dependence of the water absorbency of SAPs on the particle size and salinity was also investigated by Omidian et al.[24]

In our previous reports,[25,26] superabsorbent crosslinked poly(vinyl alcohol) and nylon 6 were prepared.

Here we report on the preparation of a superabsorbent hydrogel copolymer consisting of acrylamide (AAm) and CMC crosslinked by electron-beam radiation. The swelling behavior of the crosslinked hydrogels was studied with respect to the crosslinking density, irradiation dose, and monomer–polymer ratio. The water retention of these hydrogels was also studied through the growth of rice.

EXPERIMENTAL

Materials

A sodium salt of CMC (pure polymer) in the form of granules was supplied by El-Nasr Pharmaceutical Chemical–Prolabo (Egypt). Monomer AAm (99% pure; Merck, Germany) was used as received. The other chemicals were pure-grade and were used without further purification.

Correspondence to: S. M. Ibrahim (sayedaibrahim@yahoo.com).

Preparation of the hydrogels

Polymer/monomer mixtures (2.5 g) consisting of the CMC polymer and AAm monomer were prepared by the dissolution of various weight percentages of the polymer and monomer (90/10, 80/20, and 70/30 w/w) in 30 mL of H_2O at room temperature. *N,N*-Methylene bisacrylamide was used as a cross-linking agent. It was added at a concentration of 0.1% (w/w) to the solution with continuous stirring. The previous components were then exposed to accelerated electrons with an electron-beam accelerator (1.5 MeV and 25 kW; high voltage engineering) at the National Center for Radiation Research and Technology, Cairo, Egypt. The required dose was obtained by the adjustment of the electron-beam energy parameters and conveyor speed (2.7 m/min). The doses were 20, 30, 40, and 50 kGy.

Characterization

Determination of the gel fraction

A known weight of the hydrogel (w_0) was extracted in a refluxing system through boiling in twice distilled water for 24 h. The samples were then removed and dried in a vacuum oven at 50°C to eliminate excess water and reach a constant weight (w_1). The soluble fraction was calculated according to the following equation:

$$\text{Soluble fraction (\%)} = [(w_0 - w_1)/w_0] \times 100 \qquad (1)$$

The gel fraction is given by

$$\text{Gel fraction (\%)} = 100 - \text{Soluble fraction} \qquad (2)$$

Swelling behavior of the CMC/AAm hydrogel

A known dry weight of the insoluble part of the hydrogel (w_1) after the calculation of the gel fraction was immersed in distilled water as well as inorganic salts at room temperature for 24 h. The swollen part of the hydrogel was weighed (w_2). The dependence of the swelling on the medium, temperature, and time was determined:

$$\text{Swelling (\%)} = [(w_2 - w_1)/w_1] \times 100 \qquad (3)$$

Thermogravimetric analysis (TGA)

TGA studies were carried out with a TGA-30 apparatus (Shimadzu, Kyoto, Japan) at a heating rate of 10°C/min in air from room temperature to 500°C.

Water retention of the CMC/AAm hydrogel

Equal amounts of soil (2 kg) were placed in two polyethylene bags (A and B), and 0.5% (w/w) SAP was thoroughly mixed with the soil in polyethylene bag A. Equal amounts of rice were placed in the two bags, and equal amounts of water (400 mL) were added initially. Germination was observed after 6 days in both bags. At the end of the experiment, after almost 1 month, the growth patterns of the plants were observed.

RESULTS AND DISCUSSION

A series of preliminary experiments were carried out with the objective of obtaining the highest gel percentage by changes in the irradiation dose and AAm concentration. From these experiment, it was found that gel formation took place only at an irradiation dose not less than 20 kGy. An irradiation dose equal to 10 kGy was not sufficient for gel formation.

Gel fraction

Figure 1 illustrates the variation of the gel fraction as a function of the irradiation dose for various CMC/AAm compositions. The maximum gel fraction for all blend compositions was obtained at 30 kGy, which was designated the gelation dose. Moreover, 100% CMC showed a gel fraction equal to 71.6% at 30 kGy, which was near the value obtained in a previous work.[27] After the addition of 10% AAm to CMC, there was a decrease in the gel fraction from to 71.6 to 67.5%. A further increase in AAm caused a decrease in the gel fraction at all irradiation doses under investigation. For example, at 30 kGy, the gel

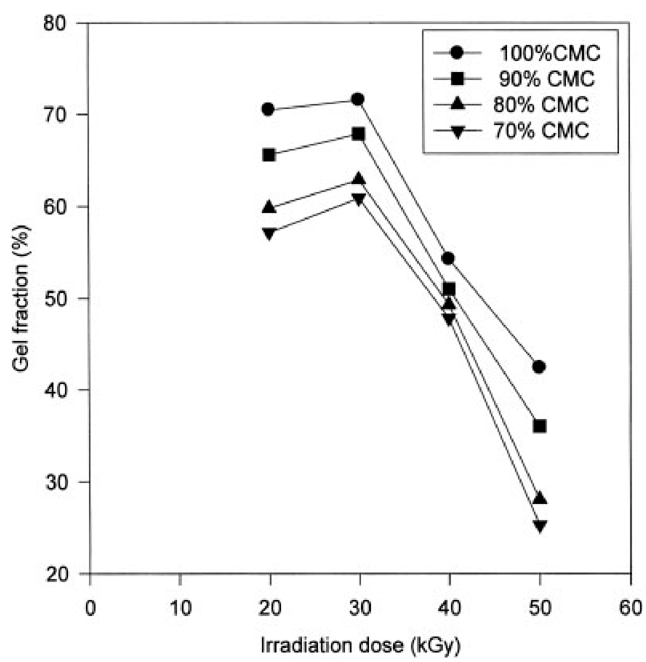

Figure 1 Effect of the irradiation dose on the gel fraction of 100% CMC and CMC/AAm hydrogels with different concentrations.

fraction decreased from 71.6 to 60% for 100% CMC and 70% CMC, respectively. The gel fractions were in the following order: 100% CMC, 90% CMC, 80% CMC, and 70% CMC. This decrease was attributed to the formation of some polyacrylamide homopolymer, which was soluble in hot water.

The decrease in the gel fraction at higher doses was attributed to the degradation processes of CMC. It has been reported that polysaccharides, including cellulose derivatives, generally degrade under ionizing radiation. However, some evidence of radiation-initiated crosslinking under special conditions has been reported.[28]

From these results, we concluded that the optimum conditions for obtaining a good hydrogel were 90/10 CMC/AAm and a 30-kGy irradiation dose.

Swelling behavior

The effect of the irradiation dose on the swelling percentage of 100% CMC and CMC/AAm hydrogels with different concentrations was studied. The results are shown in Figure 2.

The 100% CMC attained a swelling percentage lower than that attained by the other hydrogels over the entire composition range. The high gel fraction of 100% CMC resulted in a high crosslinking density, and the hydrogel became tighter and more packed. Therefore, the swelling percentage decreased.

On the other hand, for the blend compositions and 100% CMC, the hydrogels were relatively weak and vulnerable, and this made the hydrogels able to expand by absorbing and holding water in their voids. Moreover, the swelling percentages for all the samples leveled off when the irradiation increased up to 40 kGy, and then they effectively increased when the irradiation dose was raised to 50 kGy. This behavior was due to the fact that at this dose there was a marked decrease in the gel fraction that was accompanied by a high swelling percentage because of the relatively low number of intermolecular bonds between the components of the hydrogels, which permitted the diffusion of water molecules in these hydrogels.

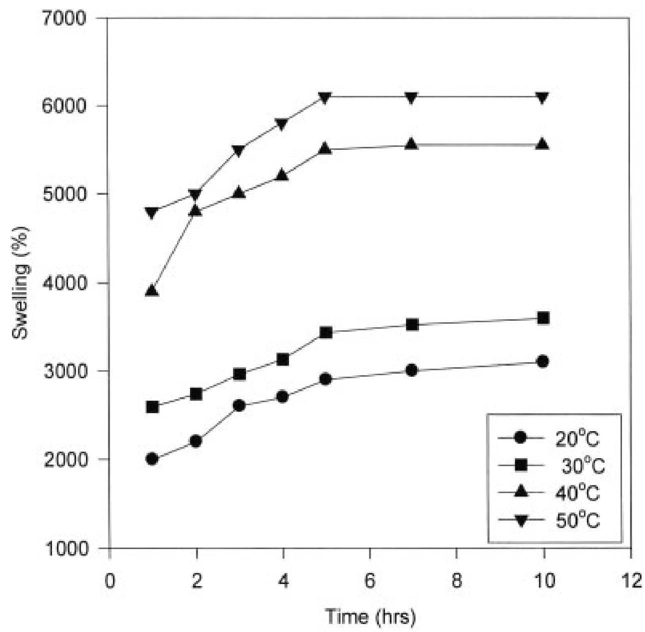

Figure 3 Effect of time on the swelling percentage of CMC/AAm hydrogels at different temperatures.

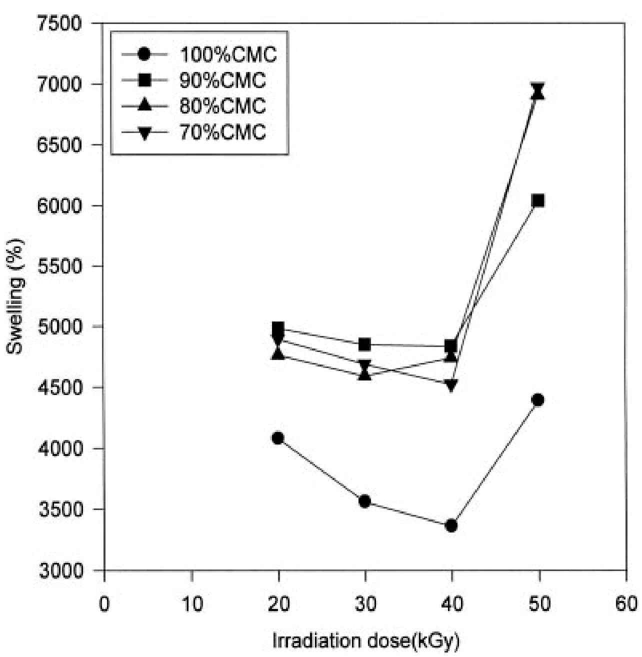

Figure 2 Effect of the irradiation dose on the swelling percentage of 100% CMC and CMC/AAm hydrogels with different concentrations with an immersion time of 24 h.

The results for the gel fraction and swelling percentage exemplify that both a high value of swelling and high crosslinking permit hydrogels to absorb and hold water.

The effects of different immersion time intervals at different temperature on the swelling percentage were studied. The results are shown in Figure 3. The equilibrium swelling percentage was attained after 5 h. Moreover, the swelling percentage increased with increasing temperature for the same time interval and also increased with increasing time at the same temperature. This trend was due to the fact that increasing the temperature caused an opening of the CMC structure, which facilitated the diffusion and absorption of water.

CMC hydrogels are very sensitive to the presence of even small amounts of salts. This can be explained by the fact that CMC is a polyelectrolyte; it has been reported that its hydrogels maintain this feature.[27] Thus, the effect of inorganic salt concentra-

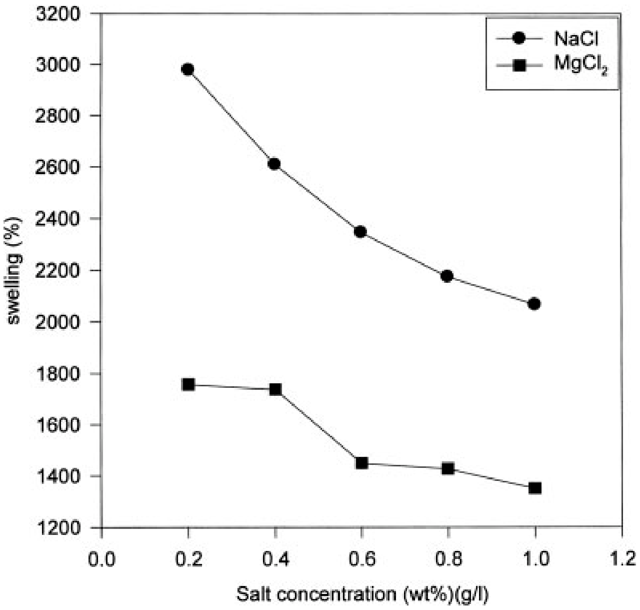

Figure 4 Effect of the salt concentration on the swelling percentage of a CMC/AAm hydrogel (90/10) at 30 kGy with an immersion time of 24 h.

tions on the swelling percentage of CMC/AAm hydrogels was studied, and the results are shown in Figure 4. As the salt solution concentration increased, the swelling percentage decreased. This can be explained by the fact that higher metal salt concentrations will restrain the extension of the tangled molecular chains of hydrogels; therefore, the swelling of the hydrogels will be inhibited.

There is a relation between the swelling percentage of hydrogels in salt solutions and the valence of the salt used. In this respect, the swelling percentage in monovalent cations is higher than that in divalent cations. This behavior has been attributed to the fact that when the valence of the metal is increased, the extension of the tangled molecular chains decreases, and this results in a decreasing value of the swelling percentage.[29]

The effects of various pH values of the solution on the swelling percentage of hydrogels are depicted in Figure 5. The optimum pH for the swelling percentage of the hydrogels was about 7. When the pH was less than 5 or greater than 8, the swelling percentage of the hydrogels decreased. At $pH < 5$, the carboxylate CooNa changed to the acid form COOH, which was less ionized. At $pH > 8$, a higher concentration of Na^+ restrained the extension of the tangled molecular chains of the hydrogels; therefore, the swelling of the hydrogels was inhibited.

Effect of different salt solutions as fertilizers on the swelling percentage

The effects of different salt solutions used in soil as fertilizers, such as ammonium nitrate, ammonium sulfate, and potassium sulfate, on the swelling percentage were studied. The results are shown in Figure 6. The swelling percentage in different salts was not affected when the salt concentration was

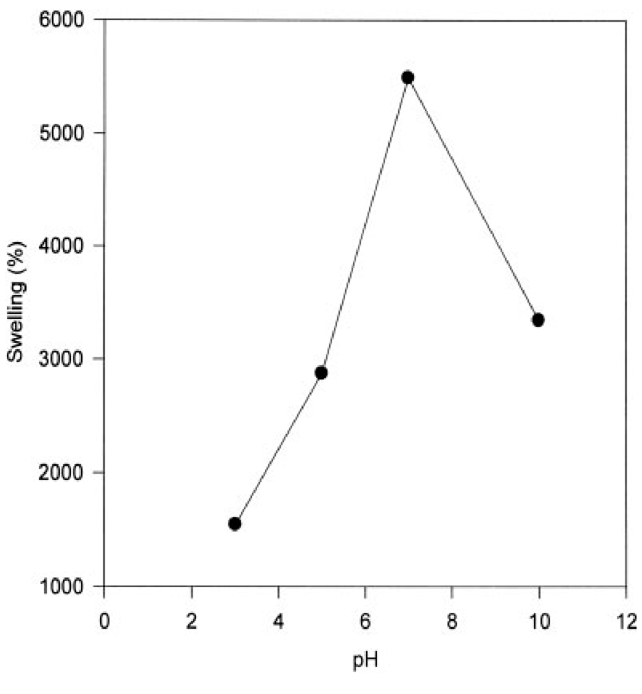

Figure 5 Effect of different pHs on the swelling percentage of a CMC/AAm hydrogel (90/10) at 30 kGy with an immersion time of 24 h.

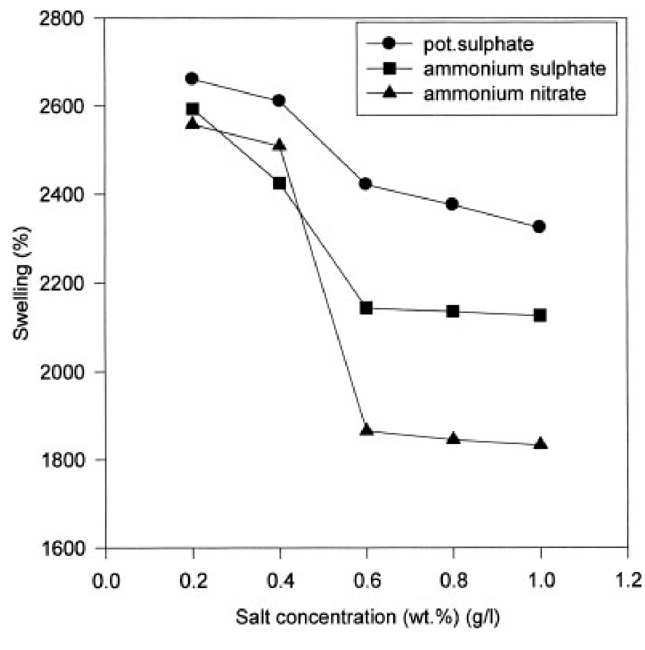

Figure 6 Effect of different salts with different concentrations on the swelling percentage of a CMC hydrogel (90/10) at 30 kGy with an immersion time of 24 h.

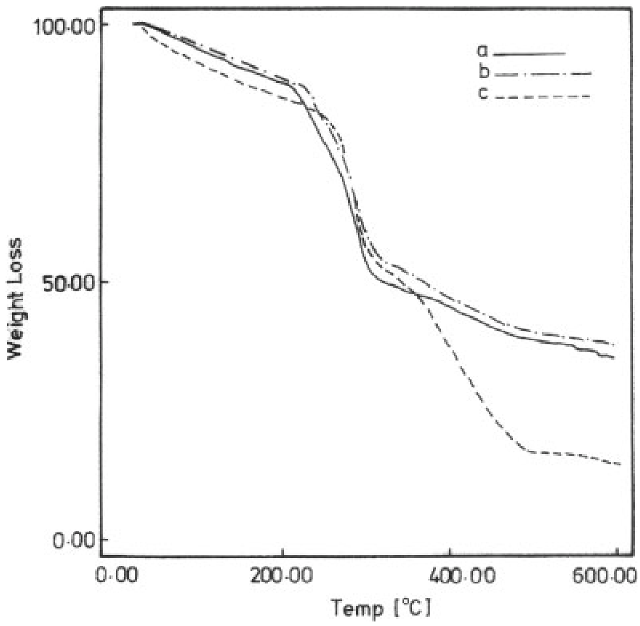

Figure 7 TGA curves of CMC/AAm hydrogels: (a) 100% CMC, (b) 90% CMC, and (c) 80% CMC.

increased up to 0.4 wt %, which was near the optimum concentration of fertilizers used in agriculture. The maximum concentration of salts (fertilizers) actually used in agriculture is about 0.5 wt % through a drop irrigation system. When the salt concentration was increased to more than 0.4 wt %, there was a reduction in the swelling ratio from 2611 to 2422 for potassium sulfate, from 2425 to 2144 for ammonium sulfate, and from 2509 to 1865 for ammonium nitrate. With 0.6–1 wt %, there was a leveling off for the three salts under investigation.

TGA

The thermal stability of the dry superabsorbent hydrogels was determined from room temperature to 600°C. Figure 7 shows the thermograms for different hydrogel compositions at various temperatures. Generally, in the initial stage of the thermograms from the ambient temperature to 200°C, the weight loss was due to the dehydration process of the water contained in the hydrophilic hydrogels. The hydrogels having concentrations equal to 100% CMC and 90% CMC showed a single-step thermogram, whereas the major weight loss of ~ 50% occurred from 200 to 300°C. This weight loss was attributed mainly to the thermal degradation of the two component polymers of the hydrogel, whereas the weight loss up to 600°C was ~ 60%. This means that hydrogels having 100 or 90% CMC showed high thermal stability. On the other hand, the thermogram of 80% CMC was a two-step thermogram. The first step was from 200 to 300°C and was accompanied by a weight loss of ~ 45%, which was also attributed to thermal degradation of the side chains. The second step took place from 300 to 500°C with a major weight loss equal to 85%. This weight loss was attributed to some thermal degradation of the main-chain C—C— bond of the hydrogel components. Apparently, the polyacrylamide contribution to the thermal degradation of the covalent bond in the last step was higher than that of CMC. This means that increasing the AAm concentration in the hydrogels caused a decrease in the thermal stability.

Water retention of the CMC/AAm hydrogels

One of the most important applications of superabsorbent hydrogels is for agricultural and horticultural purposes, especially for effective utilization of water in dry and desert regions and for the transformation of dry and desert regions into green and fertile lands.

In previous work, the water-retention test was applied to ground nuts and rice.[30] In this work, the general observation of the growth pattern of rice was undertaken and is presented in Figure 8. First, there was no considerable difference in the growth of the plants in the two bags to 15 days. After 15 days, the plants in bag B started wilting, whereas the plants in bag A were fresh. This was due to the fact that the superabsorbent hydrogel had excellent water retention. At this juncture, an additional amount (400 mL) of water was added to bag B only. Even after 30 days of growth, the plants in bag A were still fresh, whereas the plants in bag B started wilting, although an additional amount of water (400 mL) was added to bag B. Further growth of the plants was observed

(a) (b)

Figure 8 Growth patterns of rice: (a) a blank and (b) a blank plus a CMC/AAm hydrogel.

up to 40 days in both bags. Accordingly, with the aforementioned hydrogel as a superabsorbent hydrogel, the moisture content of the soil could be retained up to 1 month. Therefore, if the superabsorbent hydrogel was applied to farmland, it would act as a subminiature reservoir, retaining and supplying the soil with water. From this study, it can be concluded that water can be saved and managed in dry and desert regions, and superabsorbent hydrogels can be used for the growth of plants with less water, thereby changing drought and desert regions into green and fertile lands.

An important factor for rice is that it usually needs to be immersed in a lot of water. Therefore, the presence of superabsorbent hydrogels in the ground could reduce to a great extent the amount of water needed for irrigation because they would keep rice moist for a sufficiently long time.

CONCLUSIONS

CMC/AAm hydrogels were prepared by radiation crosslinking with an electron-beam accelerator. The gelation dose was identified and was equal to 30 kGy. The optimum concentration of CMC/AAm was 90/10. The swelling properties of the hydrogels were higher in distilled water than in inorganic salts. The swelling increased with increasing temperature. The water retention of soil was enhanced with the hydrogels. The results of this work indicate that these hydrogels possess good water-retention capacity.

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