

CONTROLLED RELEASE FROM PDMAEMA GELS PREPARED BY GAMMA RADIATION*

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Abstract Poly(*N,N*-dimethylaminoethyl methacrylate) (polyDMAEMA) hydrogels prepared by γ -irradiation showed obvious temperature-sensitivity in a temperature range of 38–40°C and pH-sensitivity at pH = 2.5. They also showed electric response behavior although it was not typical. The hydrogels were used in controlled release at different pH, temperature, and electric voltage. The release rates of methylene blue (MB) from the gels at 52°C and pH = 1.24 were faster than those at 20°C and pH = 10.56, respectively. In addition, the release rate at a field voltage of 5.0 was also faster than that without electric field.

Keywords Poly(*N,N*-dimethylaminoethyl methacrylate), Environmental sensitivity, Hydrogel, Controlled release

INTRODUCTION

A hydrogel is a kind of crosslinked polymer which can swell but cannot dissolve in water. There are some hydrogels which can modulate the swelling ratio in response to environmental stimuli such as temperature, pH, and electric field^[1–3]. Such characteristics could be used in a variety of chemical and biological separations and in controlled release^[4–8]. In recent years, the research on and development of intelligent drug delivery systems (DDS) have become intensified, so the synthesis and characteristic study of environmental sensitive hydrogels became important. The polyDMAEMA hydrogels have special structures, which are similar to *N*-isopropylacrylamide, a typical environmentally sensitized hydrogel. This indicates polyDMAEMA hydrogel might be used in intelligent drug delivery systems. These hydrogels are transparent and display good swelling behavior in water. In this work, the characteristics of the polyDMAEMA hydrogels synthesized by γ -irradiation technology, such as temperature-, pH-, and electric-sensitivity were studied and the controlled release behavior of the hydrogels was investigated.

EXPERIMENTAL

Materials

DMAEMA monomer was purchased from Acros Chemical Industries (USA) and purified by distillation under reduced pressure. Methylene blue (MB) was purchased from Chinese Medical & Drug Co. The other reagents are commercially available and used without further purification.

Characterization Measurements of PolyDMAEMA Gels

The polyDMAEMA hydrogels were synthesized by γ -irradiation as in the previous work^[9]. The swelling characteristic of the gel was measured as following:

* This work was financially supported by the National Natural Science Foundation of China (No. 39870227); this paper was reported on International Symposium on Radiation Technology in Emerging Industry Application, held on Nov. 6–10, 2001 in Beijing, China

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Received September 7, 2001; Revised October 17, 2001; Accepted October 19, 2001

$$\text{Swelling ratio (\%)} = (W_t - W_0)/W_0 \times 100\%$$

where W_t is the weight of the swollen sample with inclusive water, and W_0 is the weight of dried sample.

The electric responsive function was tested by sandwiching the swollen hydrogel between two platinum electrodes (2.2×2.2 cm) in water. The test apparatus is self-made as shown in Fig. 1. The weight change of the hydrogel which occurred after electrification was calculated by the equation:

$$\text{Weight change (\%)} = (W_g - W_0)/W_0 \times 100\%$$

where W_g , W_0 are the weight of sample after electrification and before electrification.

Controlled Release

The controlled release of MB was performed after the polyDMAEMA hydrogels reached the swelling equilibrium and saturated absorption of MB in solution. The MB concentration in solution was determined by using a UV spectrophotometer at 663 nm. The relative release of MB from hydrogels was expressed by W_t/W_∞ . Here, W_t and W_∞ were the weights measured at t and the equilibrium release state, respectively.

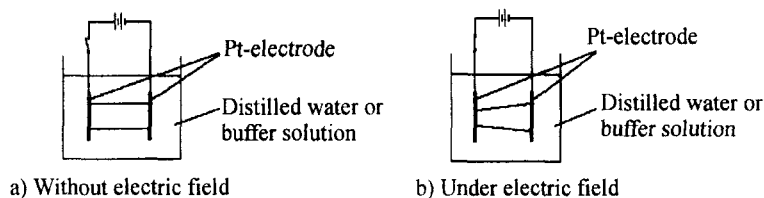


Fig.1 Scheme of apparatus for electric response

RESULT AND DISCUSSION

Optimum Conditions of Preparation by γ -Radiation

The polyDMAEMA hydrogel was obtained by γ -ray irradiation with a ^{60}Co source (Peking University, 3.7×10^{14} bq) at room temperature. Some factors which affect the radiation syntheses of polyDMAEMA hydrogels, such as absorbed dose, dose rate, concentrations of monomer and crosslinkers have been investigated in detail in previous work^[9]. The optimum preparation conditions were found to be absorbed dose = 18 kGy, dose rate = 102 Gy/min, monomer concentration = 30% (V/V) in water solution and crosslinker concentration = 1.5 g/L in water solution. The hydrogels obtained were transparent and displayed good swelling behavior.

Characteristics of PolyDMAEMA Hydrogel

The polyDMAEMA hydrogels obtained in this work show good mechanical properties and high swelling capacities in water. The equilibrium degree of swelling was approximately 900%. The hydrogels also display temperature and pH-sensitivity at 38–40°C and pH = 2.5. The results are shown in Figs. 2 and 3.

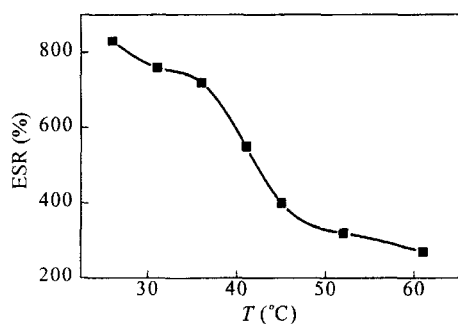


Fig. 2 Equilibrium swelling ratio (ESR) as a function of temperature pH = 6.84

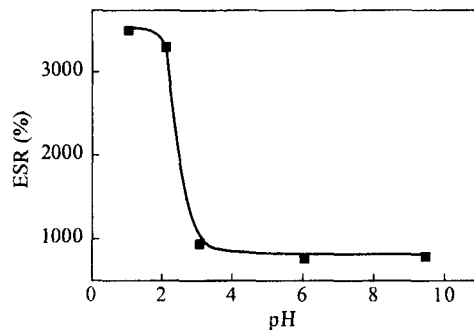


Fig. 3 Equilibrium swelling ratio (ESR) as a function of pH value at 20°C

Figure 4 shows the electric responsive behavior of the gels. Although it is not very obvious, the responsive voltage observed was at a field voltage of 3.0 V.

Controlled Release

MB release at different pH

MB release experiments were performed in deionized water at pH = 1.24 and 10.56 at room temperature. The release rate of MB at pH = 1.24 was faster than that at pH = 10.56. At pH = 1.24, it leveled off after about 13 h while at pH = 10.56 the time was about 60 h (see Fig. 5). In acid solution of pH = 1.24 the gel swelled. Thus the released MB molecules can easily diffuse out from the gel, while in basic solution of pH = 10.56, the gel shrank and MB molecules were difficult to diffuse out.

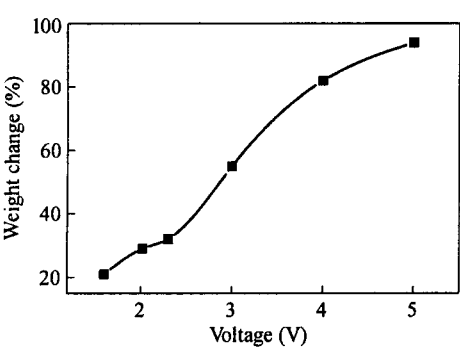


Fig. 4 Effect of voltage on the electrical response of polyDMAEMA hydrogels

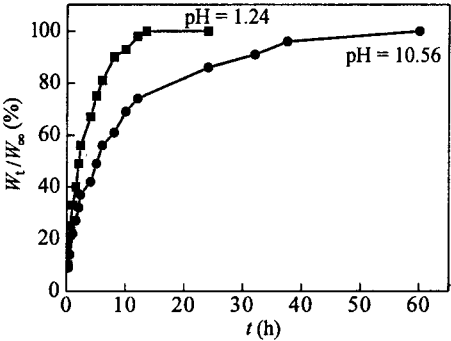


Fig. 5 The release of MB at different pH, $T = 20^{\circ}\text{C}$

MB release at different temperatures

Since the polyDMAEMA hydrogel showed temperature sensitivity at 38–40°C, the release experiments were conducted at 20°C and 52°C, respectively. The results are shown in Fig. 6. It was found that the release rate at 52°C was greater than that at 20°C, which could be attributed to the size of MB molecules. Even though the gel shrank at high temperature, MB molecules still could pass through the gel and the release rate was fast due to the fast diffusion of MB molecules at high temperature.

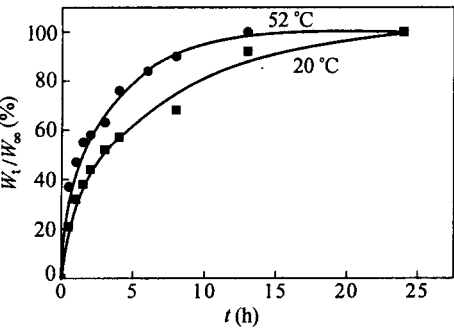


Fig. 6 The relative release of MB at different temperature when pH = 6.84

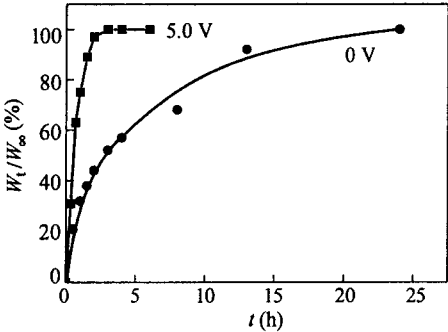


Fig. 7 MB release rate at different voltages

MB release in electric field

Figure 7 shows the release rate of MB at different electric voltages. The release rate at a field voltage of 5.0 V was much higher than that without electric field. For example, it took 3 h to reach equilibrium at a field voltage of 5.0 V. Without the electric field, it needs 23 h. However, the amount of MB in hydrogel could not be completely released at 5.0 V, while without electric field it could. Figure 8 shows the release of MB under on-off

switching of electric field in distilled water at alternating voltages 0 and 5.0 V. The released amount was indicated by the OD values of the solution. From Fig. 8, it can be seen that MB could be released from the polyDMAEMA hydrogel when the switch was on and it could hardly be released when the switch was off.

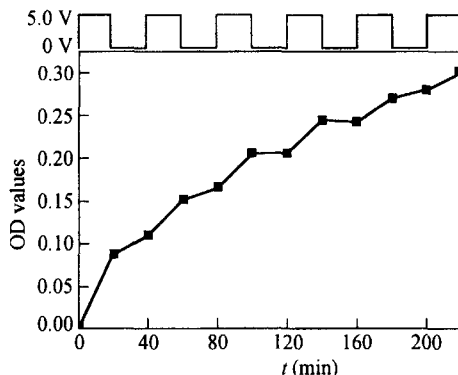


Fig. 8 MB release over time in a pulsed electric filed

CONCLUSION

PolyDMAEMA hydrogels prepared by the γ -irradiation technique exhibit obvious pH- and temperature-sensitivity at a pH value of approximately 2.5 and at the temperature range of 38–40°C. Although the electrical sensitivity of the gel was not typical, it was observed at 3.0 V.

Controlled release studies show that the release of MB at pH = 1.24 and at 52°C was faster than that at pH = 10.56 and at 20°C.

The release at a field voltage of 5.0 V was faster than that without electric field, and it could be controlled by on-off switching.

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