

STUDY ON THE SWELLING BEHAVIOUR OF COPOLYMER HYDROGEL

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ABSTRACT

The states of water in poly(N-vinylpyrrolidone-methylmethacrylate) and poly(N-vinylpyrrolidone-2-hydroxyethyl methacrylate) hydrogels have been studied by means of DSC. The effect of polymer structure on equilibrium swelling extent of water has been examined. It was found that the state of water and the water content in different hydrogels were dependent on the kind of monomer used, the component of copolymer, the sequence distribution of the monomer unit and the degree of cross-linking (including chemical and physical) to a great extent. The equilibrium water content of the hydrogel may be regarded as the sum of the different state of swollen water contents of the hydrogel. Based on these, a semiempirical formula used to estimate the equilibrium water content of the copolymer hydrogels was presented.

Hydrogel, the polymer network swollen by water, is an important category of biomedical materials^[1]. A 'three states model' was presented by M. S. John et al.^[2] during their investigation of the swelling behaviour of hydrogels. They hypothesized that there are at least three states of water in hydrogels: hydrated water; interfacial water, having a certain ordered arrangement, and finally 'normal' or bulk water. This model was supported by a series of experiment facts^[3-6]. Based on this, the swelling characteristics of poly(2-hydroxyethyl methacrylate) (PHEMA)^[7] and its effect on properties of materials^[8,9] have been studied. As to the copolymer hydrogels, the authors are not aware of any publications on the similar subject. In the present paper the swelling characteristics of poly(N-vinylpyrrolidone-methylmethacrylate) (P[VP-MMA]) and poly(N-vinylpyrrolidone-2-hydroxyethyl methacrylate) (P[VP-HEMA]) as well as the relative properties of these two copolymer systems are reported.

MATERIALS AND METHODS

1. Materials

Monomer	Resourcer	Purification method	b.p.	Refractive index
VP	BASF	Vacuum distillation	53°C/1 mmHg	$n_D^{25}=1.5114$
MMA	Beijing Chemical Plant	Vacuum distillation after removal of the inhibitor	46°C/97 mmHg	$n_D^{25}=1.4121$
HEMA	Synthesized by ourselves		68°C/2 mmHg	$n_D^{25}=1.4522$
EGDMA*	Synthesized by ourselves		82°C/1 mmHg	$n_D^{25}=1.4543$

* EGDMA means ethylene glycol dimethacrylate.

HEMA, VP-MMA, VP-HEMA solutions containing different amounts of EGDMA were prepared, then the above solutions were polymerized under the protection of N_2 according to the following conditions:

HEMA: initiated by BPO, 65°C/4.5 hr, 85°C/4.5 hr, 100°C/2 hr;

VP-HEMA: initiated by BPO-ABIN, 60°C/5 hr, 85°C/5 hr, 105°C/2 hr;

VP-MMA: initiated by BPO-ABIN, 45°C/50 hr, 60°C/24 hr, 80°C/10 hr, 105°C/2 hr.

2. Determination and expression of equilibrium water content

The polymers were cut into some $\phi 12 \times 2$ disks and dried under vacuum condition (40°C) until the weight of the sample remained constant. W_d was used to represent this weight. After that, the samples were drenched with and equilibrated in physiological saline solution (20°C). The weight of the sample at this time was represented by W_s .

Equilibrium Water Content of Polymer in Mole (EWCPM)

$$= \frac{(W_s - W_d) / \text{molecular weight of water}}{\text{mole numbers of monomer unit in the sample}} \quad (\text{mol H}_2\text{O/mol monomer unit})$$

Equilibrium Water Content of Hydrogel in Weight (EWCHW)

$$= \frac{W_s - W_d}{W_s} \quad (\text{g H}_2\text{O/g Hydrogel})$$

3. Determination of melting enthalpy of water in hydrogels by DSC

With Du Pont 910 DSC, refer to [7].

RESULTS AND DISCUSSION

1. The states of water in hydrogels and their relationships with structures

Fig. 1 represents that when the contents of crosslinking agent are different the melting

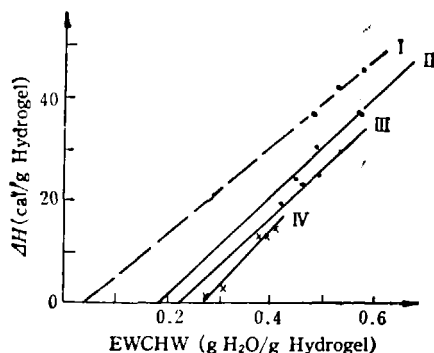


Fig. 1 Relationship between water melting enthalpy and equilibrium water content in hydrogels

- I P[VP-MMA], VP content = 80 wt%;
- II P[VP-HEMA], VP content = 45 wt%;
- III P[VP-HEMA], VP content = 35 wt%;
- IV PHEMA.

enthalpy of water is approximately proportional to EWCHW for every hydrogel. But for systems containing HEMA, when extrapolating the straight line to the zero enthalpy, the water content at this point is not zero. This means that some water in the hydrogels can not crystallize even below 0°C. This part of water is believed to be 'hydrated water' which has stronger

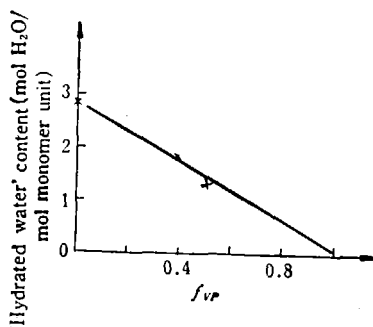


Fig. 2 'Hydrated water' content of P [VP-HEMA] hydrogels with copolymer composition

affinity with the polymer network. According to the water content at zero enthalpy, the content of 'hydrated water' can be found out. The content of 'hydrated water' is approximately zero for VP-MMA system. For systems containing HEMA, the mole number of 'hydrated water' per mole of monomer unit decreases linearly as the mole fraction of VP increases and approaches zero with pure PVP. That is to say, the 'hydrated water' is introduced by HEMA unit but not by VP unit. The reason for this behaviour is probably that the location of the

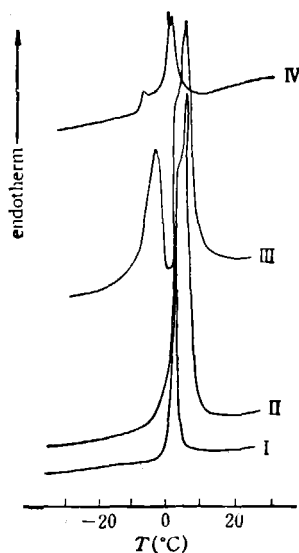


Fig. 3 DSC temperature scanning spectrum of hydrogels

I H₂O; II P[VP-MMA];
 III P[VP-HEMA]; IV PHEMA.

carbonyl in PVP chain makes the space barrier too large to form hydrogen-bond between carbonyl and water.

From the DSC spectra of these hydrogels (Fig. 3), the melting peak similar to that in nature water at 0°C can be found in the DSC spectra of each hydrogel. This peak designates the 'bulk water'. When the equilibrium water content (EWC) is low, there is only one peak in this area. But when the EWC is high, there are two closing superimposed peaks. These are caused probably by physical detaining effect. The hydrogels containing HEMA unit have another melting peak below 0°C. This peak represents the 'interfacial water'. Since this part of water is in orientation state, its melting temperature is lower than that of 'bulk water'. To sum up, three states of water do exist in the hydrogels containing HEMA unit. They are 'hydrated water', 'interfacial water' and 'bulk water'. But in the case of P[VP-MMA] hydrogels, the water in the hydrogels is almost 'bulk water'.

For P[VP-HEMA] hydrogels with different contents of crosslinking agent, the contents of 'interfacial water' and 'bulk water' can be obtained respectively from the corresponding enthalpy values. The results are showed in Fig. 4. As the amounts of crosslinking agent decrease, the 'bulk water' contents increase rapidly, but the variations of 'interfacial water' contents are relatively small. The linear relationship between the enthalpy and the EWCHW of P[VP-HEMA] hydrogels containing different amount of crosslinking agent (Fig. 1) shows that the amounts of crosslinking agent only have little influence to the 'bulk water' content if the degree of crosslinking density is not high.

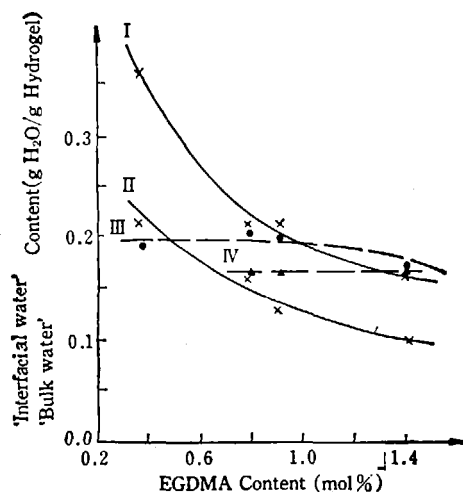


Fig. 4 The relationship between the contents of bulk or interfacial water and the crosslinking agent

- | | | |
|-----|---------------------|----------------------|
| I | VP content = 45 wt% | 'bulk water'; |
| II | VP content = 35 wt% | 'bulk water'; |
| III | VP content = 35 wt% | 'interfacial water'; |
| IV | VP content = 45 wt% | 'interfacial water'. |

2. Influential factors of equilibrium water content

Water content of hydrogel is usually characterized by the Equilibrium Water Content of Hydrogel in Weight (EWCHW) in industry. As far as the effect of polymer structure on the equilibrium water content is concerned, Equilibrium Water Content of Polymer in Mole (EWCPM) is often used. The hydrogels involved in this paper are all biomedical materials, so the solutes used here are almost physiological saline solutions except in the case of DSC tests. While physiological saline instead of distilled water is used, the equilibrium water content will vary owing to the change of the osmotic pressure, but these three kinds of swelling mechanism ought to be the same.

Fig. 5 shows the relationship between EWCPM and the components of two copolymer hydrogels. In both cases, the EWCPM increases more and more rapidly as the molar fraction of VP (f_{VP}) increases. It is obvious that the EWCPM of copolymer hydrogels is affected not only by the number and species of hydrophilic unit but also by other factors, otherwise EWCPM should be proportional to f_{VP} . After f_{VP} is greater than 0.5 in P[VP-MMA],

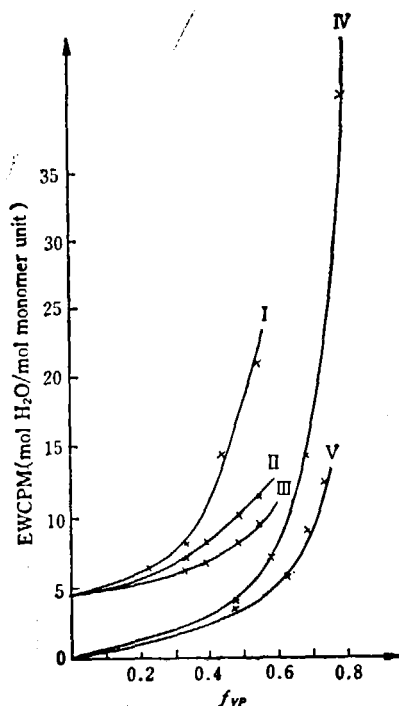


Fig. 5 Relationship between copolymer composition and equilibrium water content

- I P[VP-HEMA] EGDMA content = 0;
- II P[VP-HEMA] EGDMA content = 0.37 mol%;
- III P[VP-HEMA] EGDMA content = 0.79 mol%;
- IV P[VP-MMA] EGDMA content = 0;
- V P[VP-MMA] EGDMA content = 0.49 mol%.

EWCPM increases more rapidly. This fact illustrates at least that the sequence distribution of hydrophilic unit is another influential factor of the equilibrium water content of hydrogels. As the length of VP segment is getting longer, the swelling network becomes more extend, and possesses greater volume to hold 'bulk water'. Besides, the change of the degree of physical crosslinking is also an influential factor.

Fig. 6 and Fig. 7 represent that the EWCPM of hydrogels in various components decrease more and more slowly as the amounts of crosslinking agent increase. This behaviour is probably ascribed to the lower percentage of 'bulk water' in the hydrogels with the higher degree of crosslink.

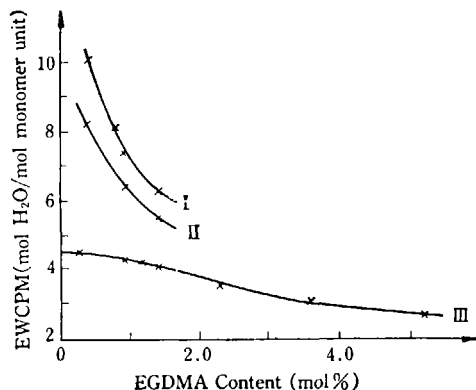


Fig. 6 Relationship between the contents of crosslinking agent and equilibrium water of hydrogels containing HEMA

- I VP content = 45 wt%;
- II VP content = 35 wt%;
- III Pure PHEMA.

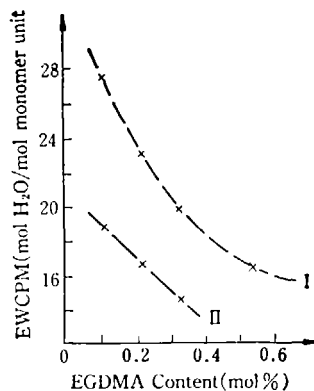


Fig. 7 Relationship between the contents of crosslinking agent and equilibrium water of P[VP-MMA] hydrogels

- I Crosslinking agent is diethylene glycol dipropenyl carbonate;
- II Crosslinking agent is EGDMA, VP content = 77 wt%.

3. Estimation of the equilibrium water content

According to the above experimental results, the effects of the polymer structure on the various states of water are not the same, and the contribution to the equilibrium water content by various states of water is also different. Based on these, it is reasonable to assume that the equilibrium water content of the hydrogel may be regarded as the sum of the different state of swollen water contents of the hydrogel.

For simplification, it is supposed that only two states of water exist in the hydrogels: 1) for strong affinity water, its content only depends on the number and the species of hydrophilic unit on the polymer network; 2) for weak affinity water, its content depends not only upon the number and species of hydrophilic unit, but also upon the length of hydrophilic segment, the chemical and physical degree of crosslink and others. Thus, monomer i binds strong affinity water $K_i f_i$, weak affinity water $F(f_i, \bar{I}_i, v, v')$ (f_i is the molar fraction of the monomer i ; $\bar{I}_i$

is its average sequence length; v, v' are chemical and physical crosslinking factor; K_1^1 and F are the coefficient and the function awaiting to be determined). According to these, we have:

$$\text{EWCPM} = \sum_i K_1^1 f_i + \sum_i F(f_i, \bar{l}_i, v, v')$$

It is difficult to derive the formula of F theoretically. But by modeling on experiment curves, a simple function is obtained: $F = K_2^1 \bar{l}_i^3 \frac{f_i^{\beta f_i}}{v + v'}$. In VP (1)-MMA (2) system, VP can not bind with water and MMA is hydrophobic monomer, therefore among the four coefficients to be determined only K_2^1 is not equal to zero. Considering the physical crosslinking is mainly caused by the hydrophobic monomer, it is reasonable to assume $v' = \alpha f_{\text{MMA}}$. By using average sequence length expression of terpolymerization and the reactivity ratios, K_2^1, α and β can be determined by means of experiment data. The following equation is obtained:

$$\text{EWCPM} = 1.044 \left(1 + \frac{f_1}{\frac{1-f_1}{0.00772} + \frac{f_3}{0.00425}} \right)^3 \frac{f_1^{8.352f_1}}{f_3 + 0.0291(1-f_1)}$$

where 1, 2, 3 represent VP, MMA and EGDMA respectively. The reactivity ratio $r_{12} = 0.00772$ (determined by experiments) and $r_{13} = 0.00425$ (calculated according to Q-e equation).

The calculated and experimental values of EWCHW were listed in Tab. 1. Most of the relative errors between the calculated and experimental values are within 5%.

Tab. 1 EWCHW of P[VP-MMA] hydrogel (cal. & exp.)

Sample number	f_1	f_3	EWCHW (cal.)	EWCHW (exp.)	Error (%)
M050	0.4973	0	0.382	0.403	5.1
M060	0.5746	0	0.507	0.547	7.2
M070	0.6776	0	0.684	0.706	3.2
M080	0.7827	0	0.857	0.870	1.6
M090	0.8902	0	0.964	1.00*	3.6
M150	0.4739	4.9×10^{-3}	0.316	0.373	15.8
M165	0.6258	4.9×10^{-3}	0.499	0.490	1.8
M170	0.6776	4.9×10^{-3}	0.586	0.598	2.0
M175	0.7299	4.9×10^{-3}	0.678	0.675	0.6
M177	0.7510	1.1×10^{-3}	0.787	0.757	3.9
M277	0.7510	2.2×10^{-3}	0.765	0.733	4.3
M377	0.7510	3.3×10^{-3}	0.745	0.707	5.4

* Completely solved

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