

Synthesis of self-crosslinking sodium polyacrylate hydrogel and water-absorbing mechanism

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In this paper, the super-absorbent, self-crosslinking sodium polyacrylate was synthesized by means of reversed-phase suspension polymerization under gamma-ray irradiation and the water-absorbing mechanism of the self-crosslinking hydrogel was revealed. Some physical parameters of such a network were estimated and investigated. The stable suspension polymerization of sodium acrylate was carried out in the presence of a surfactant complex consisting of anionic surfactant dodecylbenzen sulfonic sodium (DSS) and nonionic surfactant Span60 or Span20 with a certain ratio. The dual-electronic structure resulted from such a surfactant complex makes the dispersed monomer solution droplets a stable suspension in organic solvent. The water-sorbability was related to the radiation conditions such as dose, dose rate, and degree of monomer neutralization. Only under high dose and dose rate, some initiated branch side species on the main macromolecular chain can couple each other and cause a self-crosslinking network which may contain a lot of water. The gel dose was about 1.57 kGy (radiation dose unit), and $G(X)$, or G value expressed as crosslinking probability at certain energy of 100 eV, was calculated and found to be 2.46 (1/100 eV). The water-sorbing procedure includes three stages, e.g., sorption on the pore surface, ionization of the fixed charges in the network, and swelling equilibrium. The crosslink chain length in the self-crosslinked sodium polyacrylate network, expressed as M_c , can be calculated and related to gel dose. © 2001 Kluwer Academic Publishers

1. Introduction

Synthetic materials which can absorb 1000 times over their own weight are desired as water-retaining agents for plant growing, or medical use such as disposable diapers, tampons, sanitary napkins and the like. A lot of papers have been found to report synthesis of these polymeric materials in the past three decades years [1–14]. In 1961, Russell *et al.* [1] first reported synthesis of starch-grafting polyacrylonitrile, then Fanta [6–8] continued their study and its manufacture was realized industrially in the Henkel Company. Wistler [3] reported the developed procedure of acrylic acid-grafting cellulose through reversed-phase suspension polymerization. However, these grafting polymers could only absorb about 500 times their own weight. Another kind of material composed of crosslinking sodium polyacrylate or its copolymer exhibited the strongest water-sorbability and were studied in detail recently [9, 11–13]. The directly heat-induced polymerization of partly neutralized sodium acrylate or its comonomer usually resulted in the inter-molecular crosslinking or

intra-molecular crosslinking in presence of crosslinking agents or bridge agents, such as *N, N*-methylene bisacrylamide, bismethyl bisacrylate etc. However, the reactions are exothermic, leading to uncontrolled polymerization. Synthesis of such absorbents consisted of sodium acrylate by using high energy irradiation (e.g., gamma-ray from Co60, electronic-ray from Van de Graaff accelerator or ultraviolet ray) is interesting, as they prevent exothermic polymerization. Li [14] first reported co-polymerization of acrylamide in solution or bulk polymerization in the presence of a crosslinking agent by means of gamma-ray irradiation. These materials showed good water-sorption at 500–1000 times.

In the previous paper [15–18], we reported the stable polymerization initiated by heat, the kinetics of polymerization reaction, and the relationship between water-sorbability and reaction conditions. In this paper, we first carried out the polymerization of partly neutralized sodium acrylate under low temperature through reversed-phase suspension polymerization using gamma-rays. Hydrogel particles of self-crosslinking

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polyacrylate were directly obtained. The relationship between intermolecular crosslinking degree and dose or dose rate was established and the truly water-absorbing mechanism disclosed.

2. Materials and experimental

Acrylic acid (supplied from Gao Qiao Chemical Plant, Shanghai) was distilled under vacuum. Span20, Span60, Tween 20 and dodecylbenzen sulfonic sodium (DSS) were directly used as obtained from Aldrich. Other materials were of chemical purity provided from various manufacturers.

Neutralized sodium acrylate solution was first prepared by slowly dropping acrylic acid into a flask containing 50% of NaOH solution with strong stirring at 0°C (cooled by using ice-water bath). Then, into 250 ml a three-neck flask equipped with reflux condenser, sodium acrylate solution, hexane and surfactants were all added. The mixture was purged with nitrogen, degassed three times, then sealed in vacuum. The gamma ray source of Cobalt-60 in East China University of Science and Technology ($7.4 \times 10^{14} B_q$) was utilized for imitating polymerization at room temperature. The resulting polymer, as hydrogel-like gel-spheres was filtered out, washed thoroughly with methanol three times and then dried in an oven at 105°C more than 24 hrs. The sorbability of dry gel to various liquids like deionized water, NaCl salt solution, and other solvents, was measured by means of the Tea Bag method as follows: about 0.1 g of sample was added to a small bag made of nylon (50 mm × 90 mm) with 200 mesh., then the bag was dipped into deionized water with vigorous stirring and the increase in weight was examined every 2 minutes. So the equilibrium absorption can be expressed as follows:

$$Q = \frac{W_1}{W_0} \text{ (g/g)} \quad (1)$$

where Q is the sorbability at balance, W_0 is dry sample and W_1 is total weight of water-sorbing hydrogel. The sol fraction, S was determined using the extraction with 20% of methanol solution as solvent in a Soxhlet flask at 80°C for 48 hrs. S can be written as

$$S = \frac{(W_0 - W_2)}{W_0 \times 100} \text{ (%) } \quad (2)$$

where S is sol fraction, and W_2 is the remainder after extracting. The viscosity of the sol part was measured with Ubbelohde viscometer and molecular weight calculated according to the Mark-Houwink equation as follows:

$$[\eta] = K * M^\alpha \quad (3)$$

where $K = 6.52 * 10^{-9} \text{ m}^3/\text{g}$ and $\alpha = 0.64$ are from literature [16]. The mechanical property of hydrogel sample was determined at the rate of 0.05 m/min with Shimadzu tensile test machine according to ASTM D4018-81. The dissolving calorimetry of the sample was examined with Calorimeter (Analysis and Instrument Plant No3, Shanghai, CHP101-88). The surface

Phase inversion temperature, °C

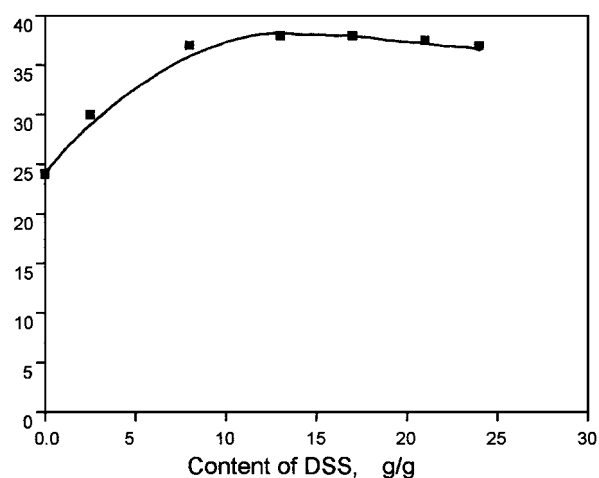


Figure 1 The dependence of PIT on the content of DSS. The total concentration of surfactant complex containing DSS and Span20 is 2.1 kg/m^3 .

area was measured at 77 K with a micromerites ASHP 2000, and calculated according to BET theory [19].

3. Result and discussion

3.1. Stable reversed-phase suspension polymerization of sodium acrylate with different surfactant complex pairs

In general, some surfactants with a suitable HLB (Hydrophile-Lipophile-Balance) value, from surfactant complexing composed of either ionic and nonionic or anion and nonionic surfactants pairs, were chosen for stabilizing reversed-phase suspension polymerization. PIT (Phase Inversion Temperature) for the monomer solution-solvent system containing surfactants complexes can be used to determine the stability. Fig. 1 shows that PIT increases gradually with increasing DSS content in complexes consisting of DSS, a anionic surfactant, and a nonionic surfactant (Span20) and then decreases. The HLB value calculated from the weight ratio value at the peak in Fig. 1 is found close to 15. But surfactant pairs consisting of different weight ratios and surfactant types with the same HLB value cause different effects on the stability of the suspension as listed in Table I. It was found that only the two surfactant complex pairs consisting of DSS and Span20 or 60 can keep the aqueous droplets suspended in organic solvent, and stabilizing the polymerization. This is because for the monomer solution-solvent reversed-phase system, most of anionic surfactant molecules can dissolve in the monomer droplets and the nonionic surfactant in the organic solvent. Anionic surfactant molecules can diffuse onto the surface of the aqueous droplets except for those partly aggregated to form micelles or rearranged to form the stable electronic structures [20] with the head of sulfonic acid group inward and the long alkyl chain outward interacting with the nonionic surfactant as schematized in Fig. 2. In the course of polymerization for such a system containing DSS and Span20, the fixed carboxyl ions on polyacrylate macromolecular chains will tend to repel the negative ion group of DSS, resulting in more anionic molecules diffusing onto the surface

TABLE I Some physical parameters of sodium polyacrylate prepared with different radiation conditions

Type of surfactants	HLB value	Amount of surfactant, wt%	Shape of resulting polymers	Absorbing properties of dry hydrogels	
				Deionized water, g/g	Saline water*, g/g
Span20	6	0.2	Lump	580	56
Span20	6	0.4	Lump	640	50
Span60	9	0.2	Lump	670	54
Span60	9	0.4	Lump	720	48
DSS	37	0.2	Lump	490	42
DSS	37	0.4	Lump	530	44
Span20/DSS	15	0.2	Particles	1240	120
Span60/DSS	15	0.2	Particles	1220	105
Span20/HTAB	15	0.2	Lump	580	56
Span60/HTAB	15	0.2	Lump	520	46
Span20/DSS	10	0.2	Large lump	890	102
Span20/DSS	25	0.2	Large particles	1040	81
Span60/DSS	20	0.2	Large particles	730	70
Span60/DSS	25	0.2	Large particles	680	61
Span20/HTAB	20	0.2	Lump	490	51

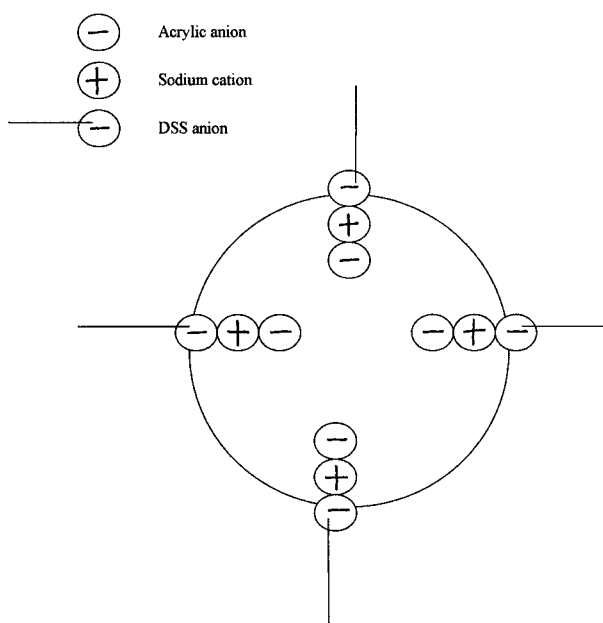


Figure 2 The schematized dual-electronic structure of the dispersed droplets.

of the droplet. These surplus DSS molecules can keep the viscous polymeric droplets from combining with each other and the hydrogel particles are obtained with a fine radius distribution as listed in Table I and Fig. 3.

Results in Table I also show that the surfactant complexes consisting of HTAB (cation surfactant) and Span20 do not give stable suspension polymerization. This is related to the ionic exchange existing in the specific electronic structure [21, 22]. The HTAB micelles can strongly bind with carboxyl anions in the monomer droplet and partly aggregate on the surface of the droplet in order to control the suspension polymerization procedure. But during the polymerization the fixed negative carboxyl ions on the polymeric chains may react with the cation head of the HTAB micelles, and the counter Na^+ ions exchange with ammonia cation of HTAB. Hence these ionic pairs which may be captured in the polymeric chains or network because of increasing viscosity of the system, will prevent the cationic

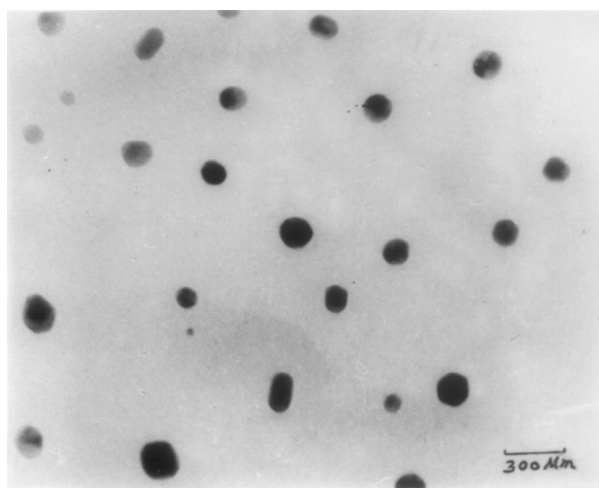
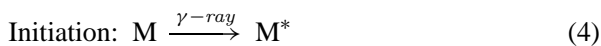


Figure 3 The micro-photo of hydrogel particles through reversed-phase suspension complex polymerization. The total concentration of surfactant complex containing DSS and Span20 is 2.1 kg/m^3 , DSS content is 20 wt%, dose is 2.34 kGy, dose rate is 0.95 kGy/hr, and neutralized degree is 90% at 18°C .

surfactants from diffusing onto the surface of viscous polymeric droplets. Then, the suspended droplets combine with each other and to induce a polymerization which is out of control.

3.2. Sorbability dependence of dry hydrogel prepared with various radiation conditions

Fig. 4 shows the dependence of water-sorbability on radiation dose. Water-sorbability increases to a peak and then decreases gradually with increasing dose. In the reversed-phase suspension system, the monomer of sodium acrylate in the suspended droplets is polymerized under irradiation according to a bulk-polymerization mechanism. The reaction mechanism can be schematized as follows:



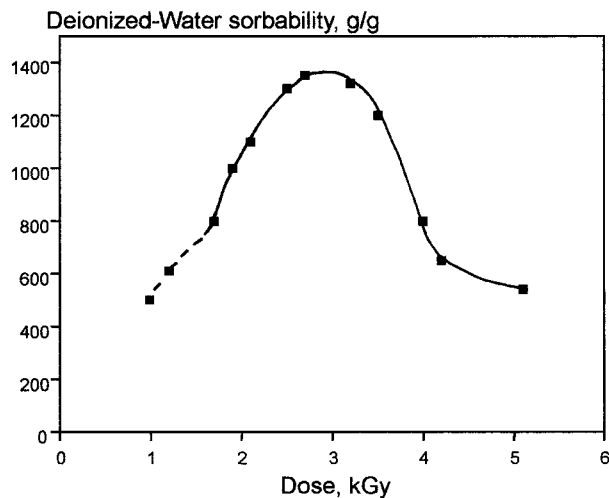
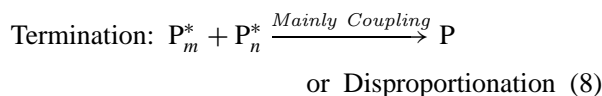
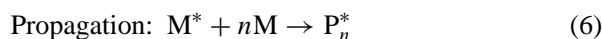


Figure 4 The water-sorbability of sodium polyacrylate dry hydrogel prepared with different dose. The total concentration of surfactants is 2.1 kg/m^3 , dose rate is 0.95 kGy/hr , and neutralized degree is 90% at 18°C .



From Equation 5 there are a lot of branched side radical sites on the main macromolecular chains initiated by gamma rays. These will propagate to form graft chains, and they can take part in binary molecular coupling reactions as Equation 8 and cause inter or intra-crosslinking reactions. The self-crosslinking effect can be enhanced with increasing the dose, resulting in a polymeric network. It can further be confirmed by the observed results of the Trommsdorff effect like the auto-accelerating phenomena during thermal polymerization in the previous work [18]. Because the increasing viscosity of the system and branch side chains decreases the diffusion rate of propagating end chains during polymerization. The concentration of free radicals sharply increases due to the collection of branch side on the macromolecular chains or chain end radical species. These radicals may promote coupling termination to form self-crosslinking chains after a period of polymerization. So, at the high dose, the higher self-crosslinking tendency can cause a shorter spacing of the network and the water-sorbability falls. However, the smaller water-sorbability or water-retaining ability obtained under the lower dose is related to defects in the crosslink network. Under low dose, the branch side species are limited and the low probability of self-linking reaction causes a lot of linear or multi short branch polymers. These polymers may dissolve in the water and can't swell to retain water, and therefore exhibit low sorbability as shown by the dashed line in the Fig. 4.

The dependence of water-sorbability on the dose rate exhibits the same tendency compared with that on the dose, as shown in Fig. 5. It is obvious that the low dose rate produces low initiation efficiency on the main backbone, giving rise to low probability of self-crosslinking.

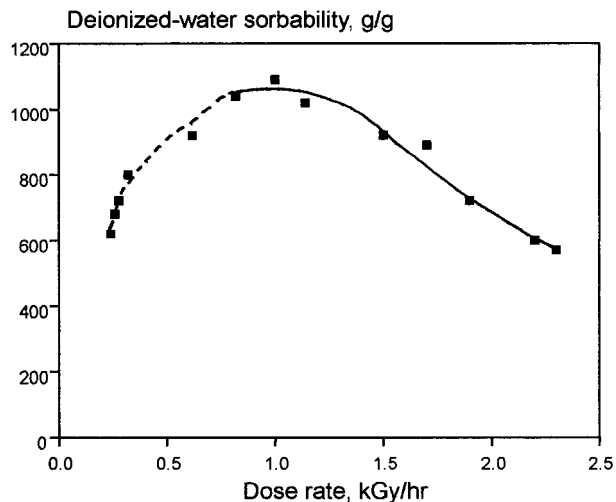


Figure 5 The water-sorbability of sodium polyacrylate dry hydrogel prepared with different dose. Rate, the total concentration of surfactants is 2.1 kg/m^3 , dose is 2.34 kGy , and neutralized degree is 90% at 18°C .

The dashed line in the Fig. 5 illustrates that no polymeric network can be formed at low dose rate and under high dose rate the low water-sorbability may be related to two facts. First, increasing branch site radicals on the macromolecular chain takes advantage of the coupling termination reaction between the intra or inter macromolecular chain, resulting in a high crosslinking degree. Second, in the high range of dose rate, the radiolysis of water is very low, so the concentration of the free radical fracture is very low. The minimal transfer reaction can take place and result in high crosslinking degree.

The crosslinking reactions as well as scission reactions take place under irradiation. Two radiation parameters, e.g. q_0 and p_0 expressed as the average number of monomer units crosslinked and average number of main chain scissions per radiation unit, respectively, will be introduced into the study. When exposed to an irradiation field, the ability of crosslinking chains can frequently be expressed as G value, e.g., the average number of crosslinking per 100 ev absorbed. For simplicity $G(x)$ (here x is expressed for any kind of crosslinking chain) is probably determined on the basis of sol-gel analysis according to Charlesby-Pinner equation [23, 24]. The sol fraction depends on the dose as follows:

$$S + \sqrt{S} = \frac{p_0}{q_0} + \frac{1}{u_1 D q_0} \quad (9)$$

where S is sol fraction, u_1 is the initial polymerization degree of crosslinking reaction and D is dose.

$S + \sqrt{S}$ plotted against $1/D$ exhibits a linear plot (see Fig. 6). The D_g , expressed as dose at the point of gelation, is obtained from extrapolating curve to $S = 1$ or $S + \sqrt{S} = 2$ and is found to be 1.57 kGy , which is very close to the dash-real cross point in Fig. 4. Then, $G(x)$ can be estimated as:

$$G(X) = \frac{4.8 \times 10^6}{D_g \times M} \quad (10)$$

where average molecular weight M of the sol part can be estimated using the viscosity-measurement of the

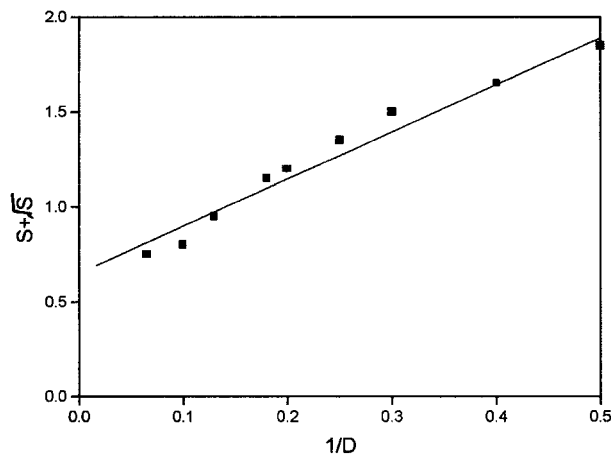


Figure 6 The plot of $S + \sqrt{S}$ against $1/D$ according to Charlesby-Pinner equation.

sol part according to the Mark-Houwink equation. So $G(x)$ is calculated and found to be 2.46 (1/100 ev) at D_g of 1.57 kGy in accordance with low crosslinking probability before the gel dose.

However, the concentration of the fixed ions in the polymeric network as well as the dimension of the network has an important effect on the water-sorbability because the swelling force of the polyelectrolyte gel usually results from the electrostatic interaction of the fixed charges on the backbone. According to Flory [25]. The net osmotic pressure in a typical Donnan equilibrium system can be approximated as shown below:

$$\pi_i = RT \left[\frac{ic_2}{Z} - v(c_s^* - c_s) \right] \quad (11)$$

where π_i is osmotic pressure, ic_2/Z is the ionic concentration in the gel, c_s^* and c_s are the concentration of external solution and mobile electrolyte, respectively and $v = v_+ + v_-$ is total molar volume of the gel ions. Then, at the balance when the total of osmotic pressure must be zero, Equation 11 can be written as the maximum swelling ratio Q instead of the osmotic pressure as a further approximation as follows:

$$Q^{2/3} \cong \left(\frac{i}{(Z - v_u)} \right) / \left(\frac{V_e}{V_0} \right) \quad (12)$$

The term $(i/(Z - v_u))$ is the concentration of the fixed charges on the dry network prior to swelling. Therefore, the system with high neutralized degree usually produces the high water-sorbability (see Fig. 7), related to the high concentration of fixed charges on the polymeric network.

3.3. Absorbing properties and mechanism

Fig. 8 exhibits the sorbability of dry hydrogel for different liquids such as deionized water, 0.9% of NaCl solution, and organic solvents. The sorbability to deionized water is 6 times more than the salt, due to the high ionic osmotic pressure when contacting outer solution (mentioned above). It is interesting that within the initial 5 minutes the deionized water sorbability attains nearly 50% of total of water-sorbability (see Fig. 8),

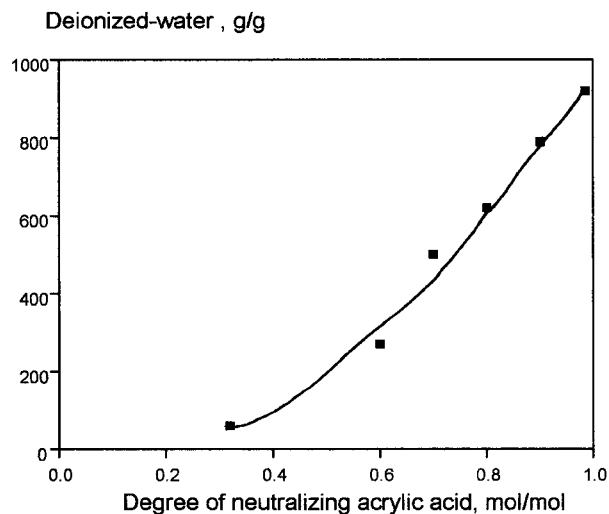


Figure 7 The dependence of sorbability to deionized water on degree of neutralizing acrylic acid. The dry hydrogel was prepared using reaction conditions identical to Fig. 3.

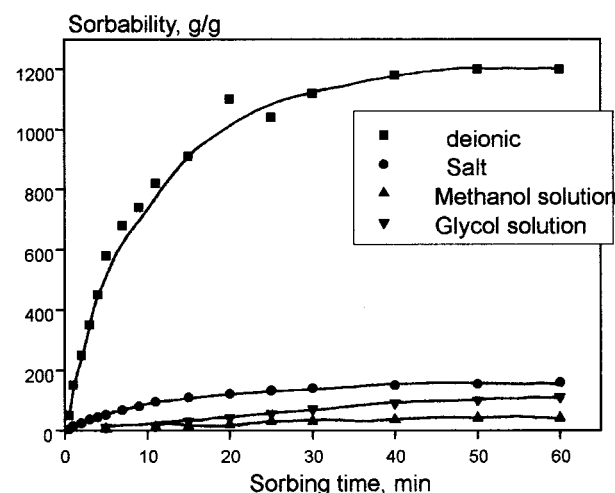


Figure 8 The sorbability of sodium polyacrylate dry hydrogel to different solvents. The dry hydrogel was prepared using reaction conditions identical to Fig. 3.

and furthermore the dry hydrogel can absorb water in the open air continuously (see Fig. 9). The facts may be partially attributed to the special surface properties. Fig. 10 indicates a lot of pores with certain radius distribution measured by means of the BET method. Furthermore, the ionization of the fixed charges with water rapidly increases the swelling ratio, which is confirmed with thermal profile measured by using calorimetry as illustrated in Fig. 11. In this case, the sorption of the small pores on the particle and the ionization with water will cause sharply increase of water absorption. Thus, the absorbing model of the ionic particle may be schematized as Fig. 12 (in fact it is the same as that reported by Loretta [26]). The part of the total water-absorbing amount is not easy to be lost even though the swollen hydrogel is dealt under high centrifugation and mechanical load (see Fig. 13a and b), related to the ionization of fixed ions in the network. However, organic solvents such as diethyl glycol and methanol can only precipitate polyelectrolyte without any ionization except for spontaneously swelling for mixing

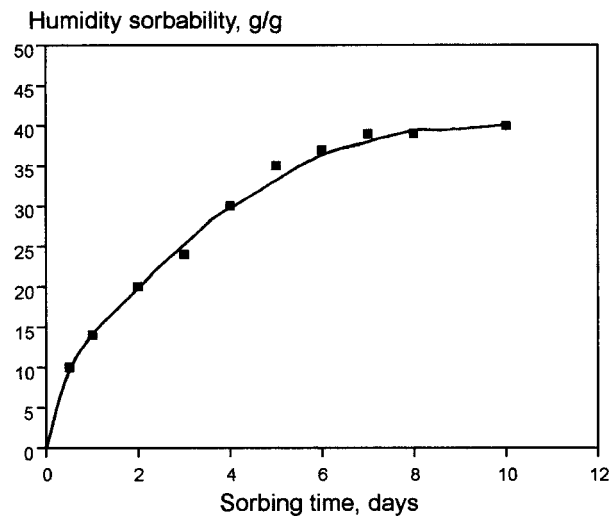


Figure 9 Humidity-absorbing effect of sodium polyacrylate dry hydrogel in the open air. The dry hydrogel was prepared using reaction conditions identical to Fig. 3.

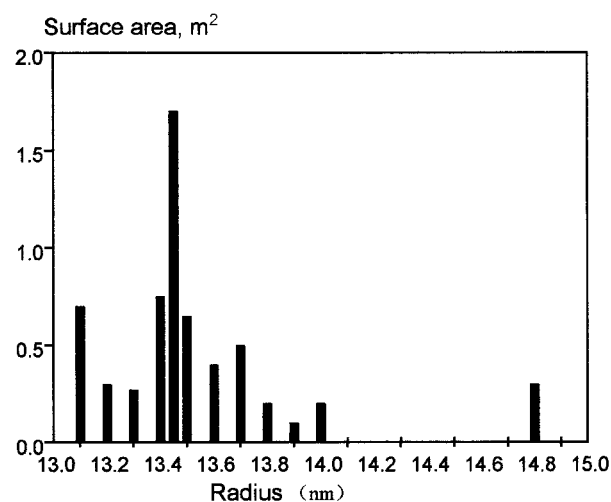


Figure 10 The surface area calculated with BET theory. The dry hydrogel was prepared using reaction conditions identical to Fig. 3.

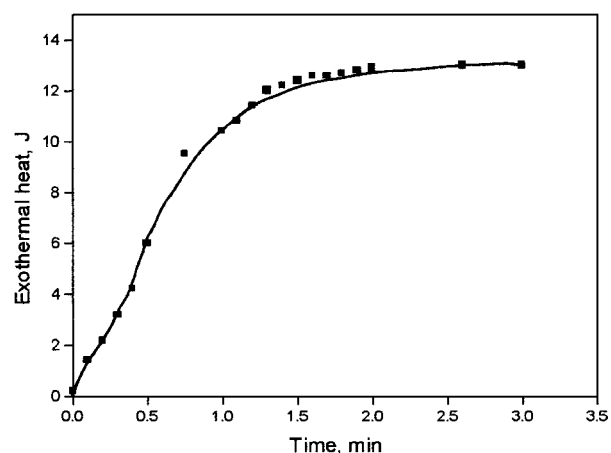


Figure 11 The profile of heat of dissolution measured with calorimetry.

entropy increasing, subject to the chain shrinkage, so the sorbability is very low.

The maximum sorbability must be related to amount of ions and the dimension of the swelling network according to Flory [25]. If the molecular weight between the two cross junction points in the network is expressed

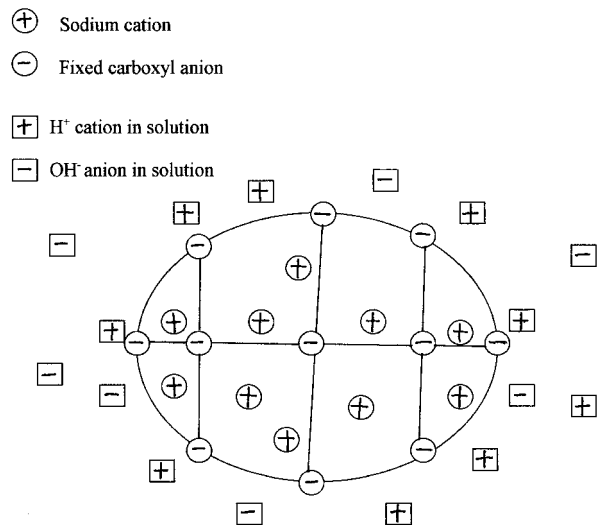


Figure 12 Ionic model of swelling of sodium polyacrylate hydrogel.

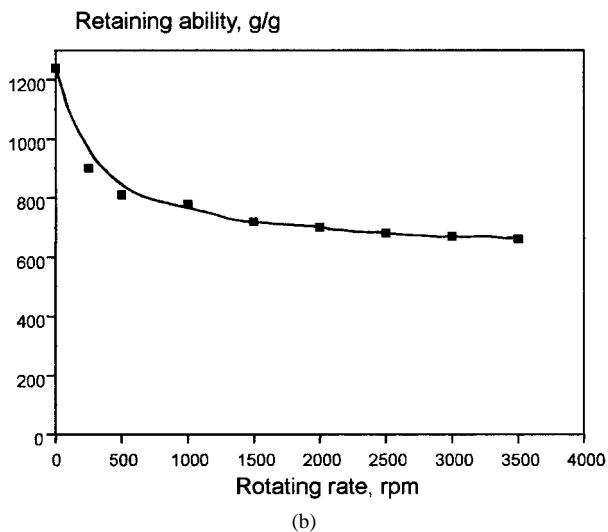
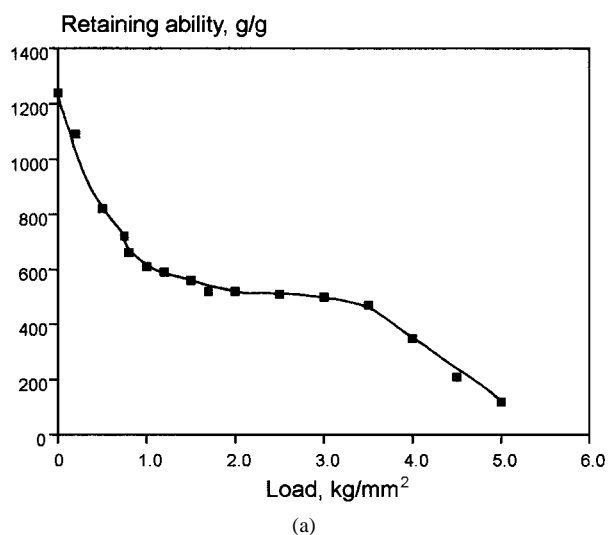


Figure 13 The swollen ionic model of sodium polyacrylate hydrogel in aqueous solution.

as M_c , it can be calculated on the basis of Nikolans theory [27],

$$\frac{\tau}{[\alpha - 1/\alpha^2]} = \frac{RTV_e}{V_0} V_2^{1/3} \quad (13)$$

where the tensile stress τ is expressed as the force per unit area of swollen hydrogel, α is the elongation ratio,

V_e is the effective molar volume per structural chain unit, and V_2 and V_0 are the volume concentration of dry and wet gels respectively. If the weight-average concentration replaces V_2 or V_0 , then,

$$\begin{aligned} \frac{\tau}{[\alpha - 1/\alpha^2]} &= RT \frac{C_{2,r}}{M_c} \left(1 - \frac{M_c}{M}\right) q^{1/3} \\ &= q_m^{5/3} RT \frac{(1/2 - \chi_1)}{V_1} \end{aligned} \quad (14)$$

where $C_{2,r}$ is defined as the initial weight concentration. Because in the case of the high swollen state the number of entanglement chains may be neglected, then the equilibrium swelling ratio can be written as follows [25]:

$$q_m^{1/3} = \frac{\left[\left(\frac{i}{2V_u S^{*1/2}} \right)^2 + (1/2 - \chi_1)V_1 \right]}{V_e/V_0} \quad (15)$$

By combining Equations 8 and 10 for elimination of V_e/V_0 , we can obtain,

$$\tau = RT \left(\frac{\alpha - 1}{\alpha^2} \right) \left(\frac{1}{2} - \chi_1 \right) V_1 q_m^{5/3} \quad (16)$$

Thus, the parameter of the interaction coefficient between solvent and polymer, called as χ_1 here, can be calculated with Equation 14 by plotting τ vs $(\alpha - 1/\alpha^2)$ as shown in Fig. 14. By substituting χ_1 in Equation 15 and other parameters given in the literature [28], the M_c can be calculated and illustrated in Fig. 15. M_c decreases sharply with increasing dose, in other words, the dimension of the self-crosslinking sodium polyacrylate network decreases consistently with the result discussed in Section 3.2 mentioned above.

In conclusion, the stable reversed-phase suspension polymerization can be carried out by irradiation and the help of a surfactant complex consisting of an anionic and a nonionic surfactants. The initiated branch site species can couple each other and cause a self-

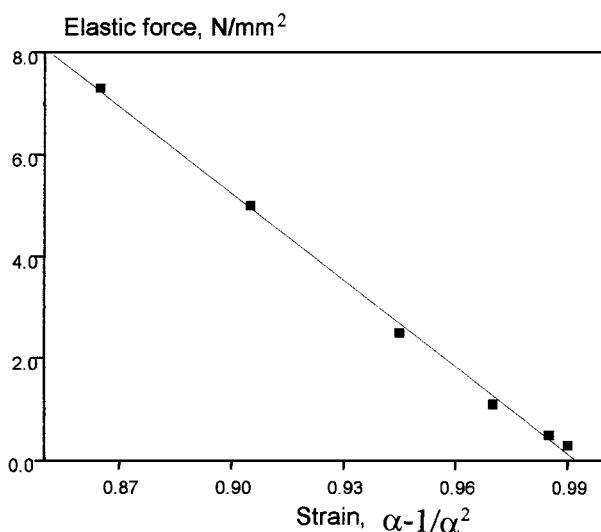


Figure 14 The plot of force τ against elongation $\alpha - 1/\alpha^2$.

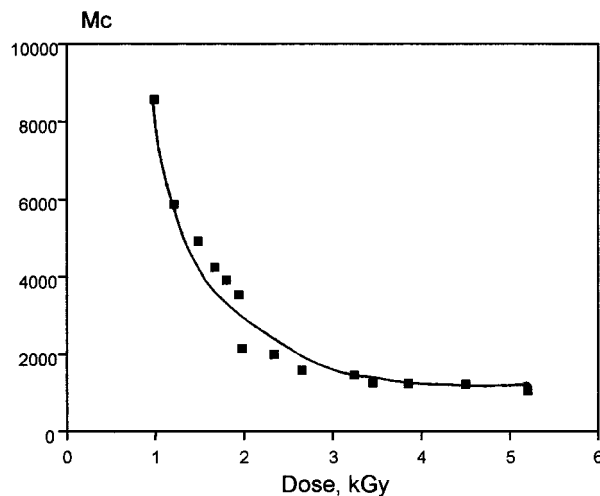


Figure 15 The dependence of molecular weight between two cross linking points, M_c on dose D .

crosslinking network. The water-absorbing mechanism can be ascribed to three stages, i.e., sorption in the pores on the material surface, ionization of fixed charges in the network, and the swelling equilibrium. The chain length between crosslinks, M_c , is closely related to dose.

Acknowledgement

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