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Synthesis Of Superabsorbent With High Absorbability From Poly(Ethylene Glycol) Methacrylate-Acrylic Acid-Acrylamide Terpolymers

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ABSTRACT

The superabsorbent resin was synthesized based on poly(ethylene glycol) methacrylate(PEGMA), acrylic acid(AA) and acrylamide(AM) by inverse suspension polymerization. By plenty of trial and error in previous works, we used mono-octadecyl phosphate as the dispersant to stabilize the suspension system effectively. In addition, the monomer we employed, PEGMA, also took a role as dispersant, this resulted in the shortage of mono-octadecyl phosphate to reduce the consumption of raw materials effectively. The effects of temperature, the concentration of monomers, the dosage of initiator, crosslinking agent and marcomonomer on the absorbency ability were studied. At the same time, the kinetics of swelling also was studied. The maximum absorption of the resin reached 930mL/g and 94mL/g for deionizing water and 0.9wt%NaCl solution, respectively.

KEYWORDS

Sodium acrylate;
Methoxy polyethylene glycol methacrylate;
Inverse suspension polymerization;
Mono-octadecyl phosphate;
High absorbability;
Swelling kinetics.

INTRODUCTION

The superabsorbent polymer was reported by the U.S. Department of Agriculture in 1961 for the first time, they are water-insoluble, hydrogel-forming polymers capable of absorbing a large amount of aqueous fluids and retaining the absorbed fluids, even under mechanical pressure. Therefore, superabsorbent polymers have great advantages over traditional water absorbing materials. Because of their excellent characters, superabsorbents are widely used in artificial snow[1, 2], agriculture[3-5], horticulture[6], drilling fluid additives[7]. Polymer concrete is suited for usage in repairing cracks[8], fighting fires[9], and sealing composites in long-distance cable and drug delivery. Later, many subsequent researches had attempted to modify these absorbent polymers to enhance their absorbency and absorption rate[9-10] later.

Poly(ethy1ene g1ycol)s(PEGs) are available as linear, end-functionalized polymers with different molecular weights from a variety of suppliers. Depending on their method of preparation, these PEGS have either hydroxyl groups at both ends or a methoxy and a hydroxyl group at the ends(MPEGs). In addition to their use in many applications as thickeners, a lot of attentions have been paid recently to these low toxicity materials in connection with applications in which PEGs are linked to biologically active molecules[11-14].

Superabsorbents based on acrylic acid(AA) have been extensively studied because AA is cheap and can achieve a polymer with a high molecular weight easily. Ionic monomers and poly(ethylene glycol)(PEO) are popularly used compounds for hydrophilicity modifications. The hydrated PEO chain can bind water to form a rapid microstream of water. Besides, PEGMA, containing the functional group PEG, show the surface activity on the one hand, which can be applied to the field of the surfactant-free dispersion polymerization. In the view of this property, we can curtail the dosage of dispersant[15-24].

In this paper, we introduced acrylamide(AM) and poly(ethylene glycol) methacrylate(PEGMA) into system for improving the properties of salt-resistance, and discussed the influences of synthesizing condition on swelling behaviors in deionized water and various salines. In our research, the dosage of dispersant was only one-fifth of other else, and this was attributing to the addition of PEGMA.

EXPERIMENTAL

Materials

Analytically pure chemical reagents were purchased from the following company: Acrylamide(AM) and cyclohexane(Tianjin Bodi Chemical Factory, Tianjin, China), Acrylic acid(AA)(Guoyao Chemical Reagent Co., Shanghai, China), N, N'-methylene bisacrylamide (NMBA)(shanghai chemical reagent co.) as crosslinking agent, Potassium persulfate ($K_2S_2O_8$)(Wuxi minfeng reagent co.) as initiator, PEGMA (Mw= 2080,Commercial pure, cognis Germany). Mono-octadecyl phosphate was prepared as reported previously[23] which as inverse suspension stabilizer.

Inverse suspension polymerization

A 100-mL three-necked flask, equipped with a condenser, a stirring rod and N_2 inlet, was charged with 24mL of cyclohexane and 0.024g of mono-octadecyl phosphate. Air was flushed from the reactor by the introduction of nitrogen until the entire process was completed. The stirrer speed was maintained at 200rpm. The temperature was set at 70^{0}C. The 80% of AA was neutralized by NaOH solution in beaker. Appropriate amounts of AA,PEGMA,$K_2S_2O_8$ and NMBA were introduced into the NaAA monomer solution, and the mixture was stirred until the materials were dissolved completely. After the inverse suspension stabilizer dissolved(continuous phase), then the 8mL of monomers solution which was sucked from the beaker, was introduced into the reactor. The polymerization was last for 2h.After the reaction, the suspension solution was cooled. The product was filtered and washed three times by ethanol. The product was then dried in a vacuum oven at 90^{0}C for 6h. White powdered polymer was obtained.

Measurement of water absorbency

Filtration method

The sample(W_{dry}) was immersed in 200mL of deionized water or 0.9wt% $NaCl_{solution}$ for at least 2h to reach swelling equilibrium at room temperature. The residual water was filtered by a 100 mesh standard screen for 15min. The volume of residual water was measure, and the equilibrium absorbency(Q_{eq}) was calculated by the following equation:

$$\mathbf{Qeq} = \frac{\mathbf{V_0 - V_{re}}}{\mathbf{W_{dry}}}$$

Where W_{dry} is the mass of the dried sample, V_0=200mL and V_{re} is the volume of the residual water.

Measurement of absorption rate

Graduate method

The dried sample(0.2g) was put at the bottom of the graduate. Deionized water(250mL) was introduced into it and timed synchronously. Then put a piece of filter paper into the graduate. When it touched the sample, recorded the time and the volume which was pointed by the filter paper. Then measure the volume per a few minutes. The absorbency(*Q*) at regular intervals was calculated by the following equation:

$$\mathbf{Q} = \frac{\mathbf{V}}{\mathbf{W_{dry}}}$$

V is the volume which was point by the filter paper; W_{dry} is the mass of the dried sample.

RESULTS AND DISCUSSION

Effect of reaction temperature

TABLE 1 : Effect of temperature on product character

temperature /^{0}C	Product form	Absorbency/mL*g^{-1}	
		Deionized water	0.9%NaCl solution
60	liquid	-	-
65	dope	-	-
70	translucent grain	347	58
75	translucent grain	424	67
80	explosive polymerization	-	-

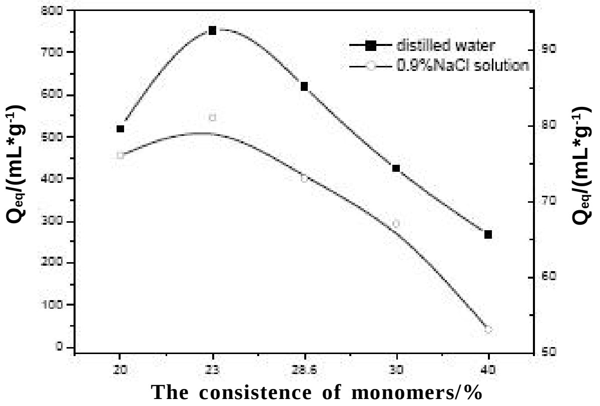

Figure 1 : Water content of copolymer with various monomer concentrations

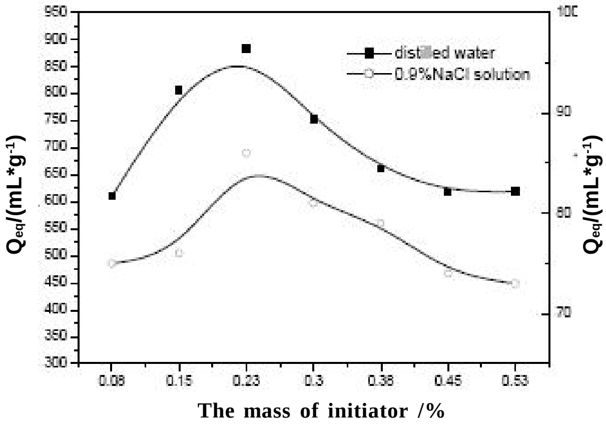

Figure 2 : Water content of copolymer with various initiator ratios

In our experiments, the molar ratio of AA, AM and PEGMA was 45:45:2, the amount of initiator($K_2S_2O_8$) was 0.3wt%(based on the mass of AA and AM), and the crosslinking agent(NMBA) was 0.03%.The polymerization was studied in a series of temperatures. The result was showed in TABLE 1.

As shown in TABLE 1, the product was liquid below 70^{0}C. Mostly the lower reaction temperature is, the initiation is ineffective and there is poor conversion. On the other hand, high temperatures(80^{0}C) lead to explosive reaction. Comparing with the two products obtained at 70 and 75^{0}C, we chose 75^{0}C as the reaction temperature for other experiments.

Effect of the concentration of monomer aqueous solution

As shown in figure1. In lower concentration (<23%), the water absorbency increased with the increase of concentration. In this atmosphere, the collision probability between monomers and active points was low; this resulted in slow reactive speed. The products with small molecular weight and slight crosslinkage were soluble partially. However, at higher consistence, above 23%, the water absorbency decreases with an increase of consistence. The quantity of heat produced in polymerization became more and more with the increase of consistence. The high temperature limited the molecular increasing, and made the resin self-crosslink gravely. So the optimal value of the concentration of monomer was 23%.

Effect of the amount of initiator on absorbency ability

Figure 2 showed that absorbency reached maximums when the mass of initiator was 0.23%(compare to the total mass of AA and AM). It was known that monomer conversion increased as the concentration of initiator increasing, so that absorbency increased while M_{KPS}%<0.23%. But with an increase in amount of initiator, the collision between monomer and free radicals also increased, which led to the increase of the soluble parts; thereby absorbency decreased, while M_{KPS}%>0.23%.

Effect of the amount of crosslinking agent on absorbency ability

The effect of the usage of crosslinking agent on water absorbency for copolymer gels is shown in figure 3. In distilled water and 0.9wt% NaCl solution, the water content of the copolymer increased with an increasing degree of crosslinking in the copolymer, when the mass ratio of NMBA is under 0.035% of the total mass of AA and AM. However, the water absorbency decreases remarkably when the mass ratio of NMBA increased from 0.023% to 0.05%. This phenomenon obeys the P.J.Flory theory[4,12]: the water absorbency is also related to the elastic force between the polymer chains. The larger the crosslinking density, the stronger the elastic

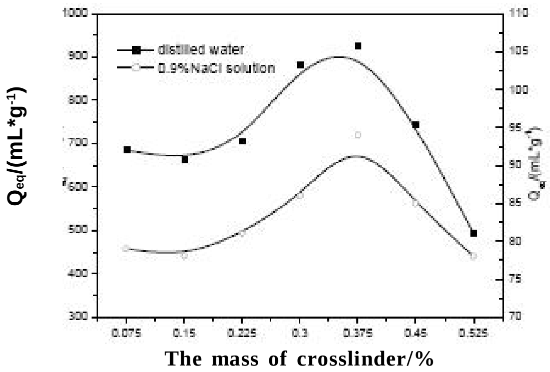

Figure 3 : Water content of copolymer with various cross linking agent ratios

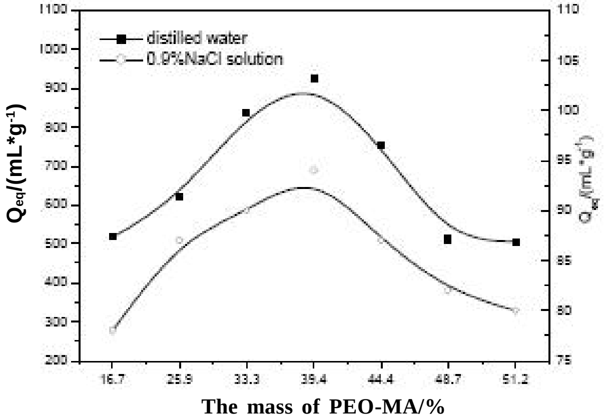

Figure 4 : Water content of copolymer with various PEGMA ratios

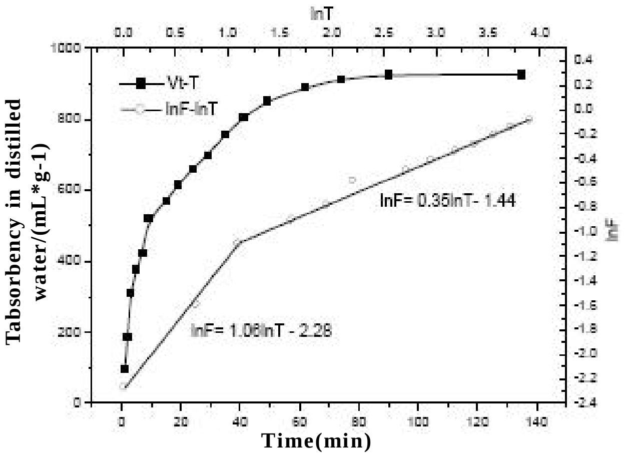

Figure 5 : Absorption rate in deionized water

force of the polymer chain, and the water absorbency is lower accordingly. In general, crosslinking agents have been employed to help improve the gel strength of the swollen gel, but they are also very effective in reducing the water absorbency.

Effect of the amount of PEGMA on absorbency ability

PEGMA was the main monomer in this study. As shown in figure 4, absorbency reached maximums when the mass of PEGMA was 39% of the total mass of monomers. The absorbency didn't decrease while non-ionic group came in because of the cooperative effect. However, the absorbency decreased remarkably when the mass was up to 39%. Because of a low reactivity ratio of PEGMA, too much PEGMA would reduce the concentration of active monomers, lead to low crosslinking density and the increase of the soluble parts.

Kinetics of swelling[24]

Measure the absorption rate of the best sample (Q_{eq}=930g/mL). Figure 5 showed that the absorbency was up to 460g/mL(50% of Q_{eq}) after 8min and 92% of Q_{eq} after 50min. To explain the process of swelling, we based on following equation:

$$F = \frac{V_1}{V_\infty} = KT^n \rightarrow InF = InK + \eta InT$$

Where T is swelling time, V_t is swelling at time, V_8 is equilibrium swelling, F denotes the amount of solvent fraction at time T, K is a constant incorporating characteristics of the macromolecular network system and the penetration, and n is diffusion exponent, which was indicative of the transport mech-anism or the type of diffusion. **(1)** n<0.5,Fic- kian diffusion, chain move fast enough that the diffusion of small molecule is the point; **(2)** 0.5<n<1.0,non-fickian transport, chain looseness and the diffusion of small molecule both work on the swelling; **(3)** n≈1.0, Case-II transport, chain looseness is the point of absorption rate. This equation was applied to the initial stages of swelling and plots of lnF verses lnT are also presented in figure 5. As shown in figure 5, in the beginning 3min of swelling, n≈1; the chain movements control the absorption rate. 3~50min, n<0.5, the water molecule diffusion become main factor of swelling.

CONCLUSIONS

(1) The system of preparing AA/AM/PEGMA copolymer by inverse suspension polymerization is simple and stable. The product is fine and well-proportioned.
(2) In our research, PEGMA shows the surface activity in inverse suspension polymerization besides advancing the salt-resistance of products, which can short the dosage of dispersant largely.

(3) Find out the best synthetic condition: 75^{0}C, the monomer consistence is 23%, the mass of initiator and crosslinker is 0.23% and 0.037%(based on the total mass of AA and AM), and the mass of PEGMA is 39% of the total mass of monomers. In this condition, the absorption amount of resins we got reached 930mL/g in deionic water and 94mL/g in 0.9%NaCl solution respectively.

(4) The resin we prepared in the best condition could absorb 460 times deionizing water than itself in 8min.The swelling process: Case-II transport in the first 3min, and Fickian diffusion from 3 to 50min.

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