Synthesis and Characterization of Acrylic-Based Superabsorbents

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SYNOPSIS

This paper is devoted to the synthesis and characterization of superabsorbent polymers based on acrylic acid. These hydrogels were prepared by carrying the inverse suspension polymerization in an aromatic hydrocarbon. The dispersion is stabilized by the mixture of micromolecular and macromolecular emulsifiers. To obtain high swelling and appropriate absorption kinetics, parameters such as initial monomer and cross-linker concentration, range of neutralization, monomer addition rate, temperature, initiating system, stabilizing system, and nature of the organic phase were studied but not reviewed here. Thus, based on these topics a basic formula is obtained to display the effect of some structural parameters on behaviour of superabsorbents utilized. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Inverse suspension polymerization involves the dispersion of a water-soluble monomer in a continuous organic phase. The latter can be either paraffinic or aromatic. Emulsifier levels are typically 2–5 wt % of the organic phase and are below the critical micell concentration (CMC). Inverse micelles have not been detected with nucleation and polymerization proceeds within the monomer droplets. The dispersion is thermodynamically unstable and requires both continuous vigorous agitation and the addition of a low hydrophilic–lipophilic balance (HLB) steric stabilizer. This forms a condensed electrically neutral interfacial layer and prevents coalescence. The monomer droplets are typically 1–100 microns in diameter and are controlled predominantly by the Weber number of the mixture. Initiation is most often carried out chemically with free-radical azo or peroxide species. These can be located either in the dispersed (aqueous) or continuous (organic) phases. If water-soluble initiators are employed, each particle contains all the reactive species and therefore behaves like an isolated microbatch polymerization reactor with the kinetics proceeding according to the solution mechanism. Oil-soluble initiators are however more common because they generate higher molecular weights and offer better thermal stability and reactor control.[1] To run inverse-suspension polymerization, three thresholds (thermodynamic, driving force, CMC) must be taken into account.

EXPERIMENTAL

In order to perform the initial work a basic formula had to be defined. A combination of orientation experiments and trials and careful evaluation of the numerous patents led us to the following.

Process Description

Preparation of the dispersed phase: A predetermined amount of aqueous caustic Solution is carefully added (dropwise under cooling) to the acrylic acid in order to obtain a partial neutralization degree. Later on, defined amounts of water-soluble initiator (potassium persulfate) is dissolved in the above-mentioned monomer solution under nitrogen bubbling until a clear mixture is obtained.

Preparation of the continuous phase: Toluene is selected as an organic phase. The organic phase containing an appropriate proportion of water in oil

Figure 1 SEM of grounded superabsorbent without modification of particle size.

Figure 3 SEM of coated particles after modification with macromolecular stabilizer.

surfactant (Span 80: sorbitan monooleate) is heated to 50°C while bubbling nitrogen into the liquid medium over a 15-min period. After preparing the two phases, a suitable amount of the oil-soluble cross-linking agent (ethylene glycol dimethacrylate) is dissolved and added to the continuous phase.

Polymerization: A four-necked flask fitted with a reflux condenser, a drip funnel, and a thermometer was used. The reactor was heated in a stream of nitrogen to 80°C and then the organic solution is poured into this.

The monomer blend was added dropwise at a predetermined flow rate to the continuous phase while the agitation speed was set at around 400 rpm. The reaction mass was left standing for 1.5 h to ensure full consumption of the remaining monomers. The water was then removed from the polymer by methanol and a drying process is employed for 24 h at 50°C in an air oven.
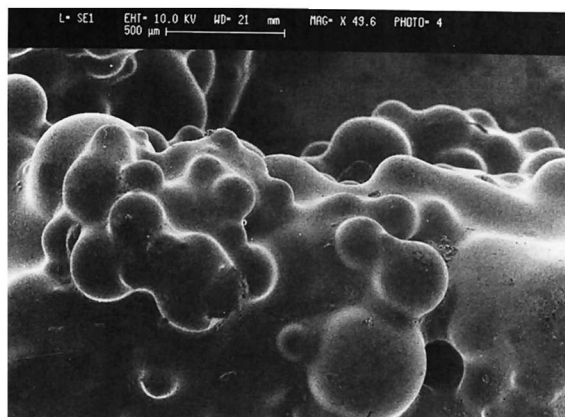
The amounts of materials used and some characteristics of the system are acrylic acid neutralization degree: 75%; monomer concentration: 46.5% (based on aqueous phase); cross-linker concentration: ranging from 0.0545 to 4.58% based on acrylic acid; initiator concentration: 0.5%/acrylic acid; surfactant concentration: 0.33%/organic phase; weight ratio of oil versus aqueous phase: 3 : 1. For all the polymerizations the monomer feed rate had been set to 10 g/min to allow isothermal polymerization.

Particle size is a key parameter in both synthesis and application of superabsorbents. Particle size distribution of the polymer was found with sieve analysis. A set of sieves was used with apertures of 300, 250, 180, 150, 106, 75, 53, 45, and 38 microns in diameter. The data obtained from the sieve analysis were used to determine the mean surface diameter of the particles (d_s).

Figure 2 SEM of lumps obtained from dispersed system shown in Figure 1 without grinding.

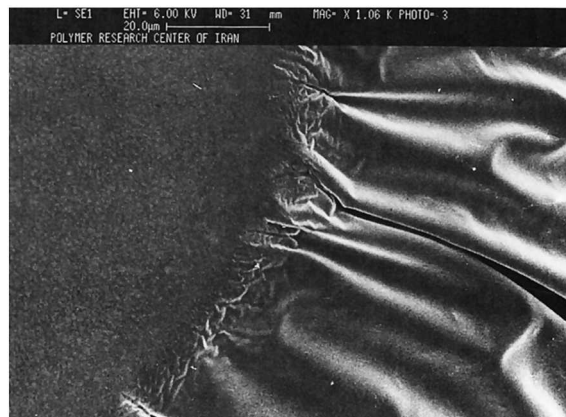**Figure 4** SEM of the boundries between polymer and stabilizer on the particles.
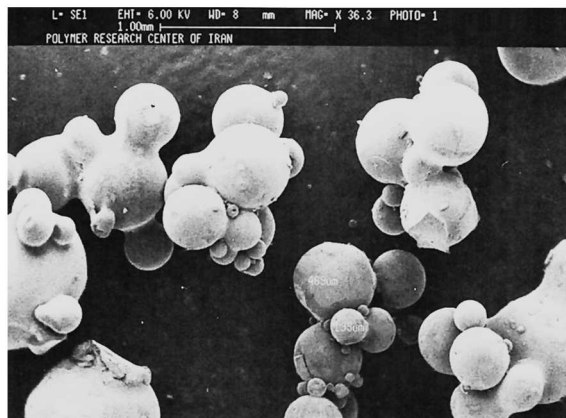
Figure 5   SEM of washed superabsorbent particles.

$$d_s = \frac{\sum pi}{\sum pi/di}$$

where pi = mass of the fraction and di = mean aperture diameter of the two successive sieves. To characterize obtained hydrogels the simple fast method is free swell determination. The aim of studying the free swell behaviour was to quantify the influence of the cross-link density or network chain density on the swelling ratio in distilled and saline water.

To run the experiment, 1 g of a superabsorbent resin was dispersed into 1500 mL of double-distilled and saline water (with different concentrations of sodium chloride) and allowed to swell sufficiently under moderate agitation. After 30 min the dispersion was filtered through a 100-mesh wire gauze and dried with a piece of soft polyurethane foam. The
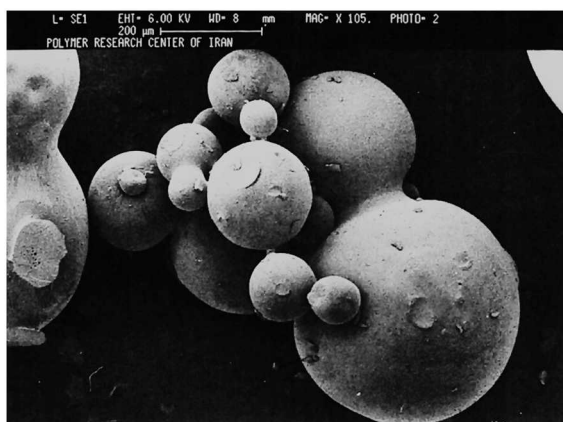

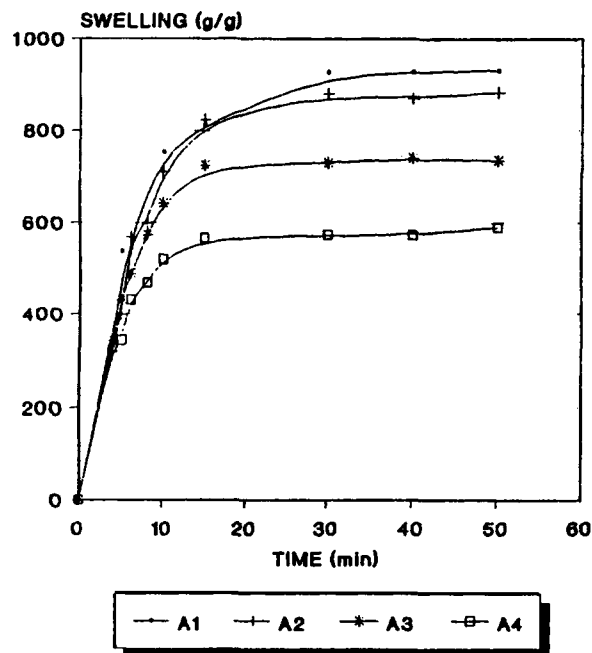**Figure 6**   Higher magnification of the particles shown in Figure 5.

Figure 7   Amount of swelling versus time.

weight of the swollen resin obtained was measured as the water absorbency of the resin.

RESULTS AND DISCUSSION

Under conditions mentioned in the Experimental Section, superabsorbent resin lump-like beads
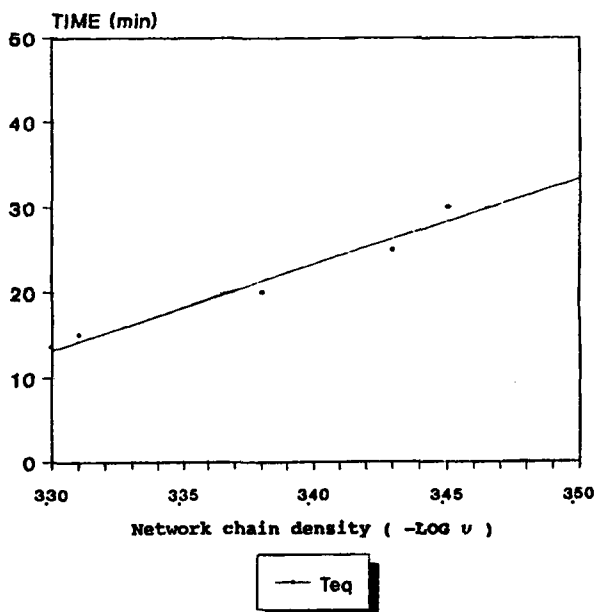

Figure 8   Time required to reach equilibrium swelling versus network chain density.

Table I   Typical Structural Properties of Hydrogels

Code of Product	A1	A2	A3	A4
Molar percent of crosslinker to monomer	5.4545×10^{-2}	2.3757×10^{-1}	2.2963	4.5836
Degree of swelling	929	880	732	578
Polymer volume fraction in the gel	6.9618×10^{-4}	7.3496×10^{-4}	8.8343×10^{-4}	1.1185×10^{-3}
Crosslink density (mol/cm^3)	1.7691×10^{-4}	1.8346×10^{-4}	2.0758×10^{-4}	2.4325×10^{-4}
Network chain density (mol/cm^3)	3.5382×10^{-4}	3.6692×10^{-4}	4.1516×10^{-4}	4.865×10^{-4}
Network chain molecular weight (g/mol)	4366	4210	3721	3175

(consisting particles of 50–500 microns) with the average particle size of 2–3 mm are obtained (Figs. 1, 2). The unique possibility of regulating the desired final particle size requires a careful selection of both nature and proportion of a stabilizing mixture associated with a suitable agitation system (geometry and speed). To obtain both high reasonable rate and capacity, optimised efficiency in retaining fluid, and safe processability characteristics, a large particle size (> 200 microns) is generally preferred.[2] By varying the micromolecular surfactant concentration (Span 80) these needs cannot be pursued and some trials must be made with macromolecular stabilizing systems. Among these types of stabilizers, ethyl cellulose (degree of substitution ranging from 2.42 to 2.53, N-14 type of Hercules) is selected. Figure 3 shows protection of the particles from adhering to each other. A layer of ethyl cellulose is coated on

the particles and because of water removal after drying is shrunk. Figure 4 displays this phenomena with higher magnification. By using this type of macromolecular stabilizer the mean surface diameter of the particles of about 300 microns is obtained (Figs. 5, 6).

According to the swelling measurements, weight swelling ratio of the hydrogel obtained without modification of particle size is about 750 g/g (for the lowest amounts of cross-linker used) and has an average particle size of 100 microns with undesirable stability because of adhering of the particles.

Some typical structural properties of the superabsorbents synthesized in this center are reported in Table I. Details about deriving structural parameters are reported elsewhere.[3] The samples of A1–
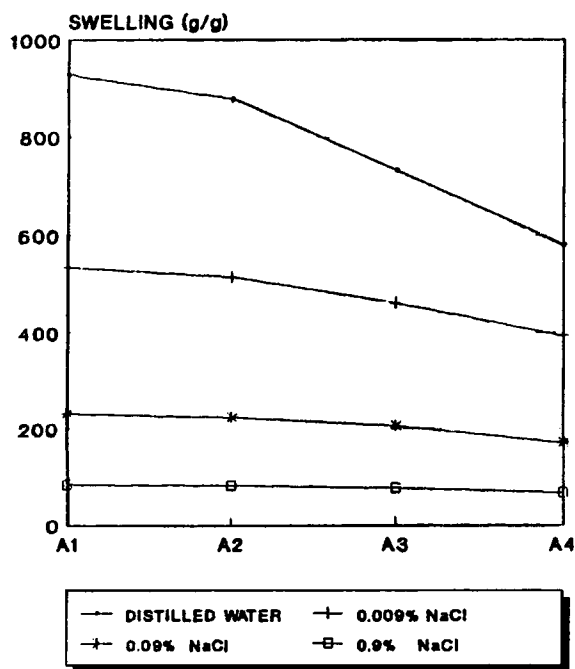
Figure 9   Variation of swelling.
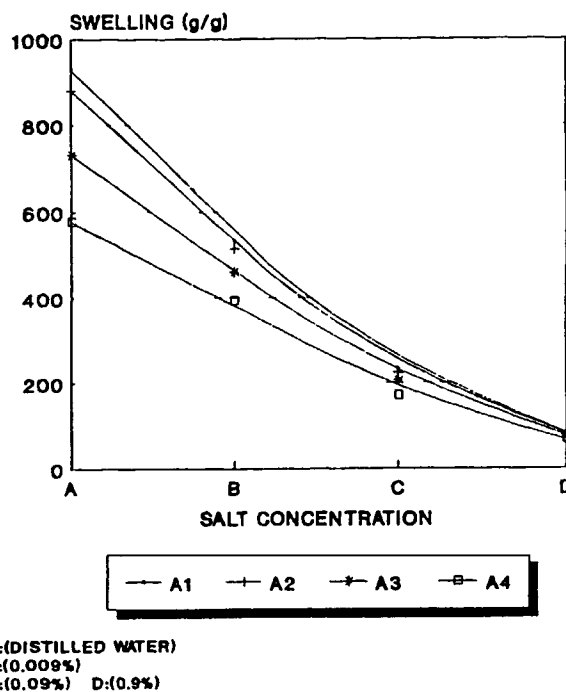
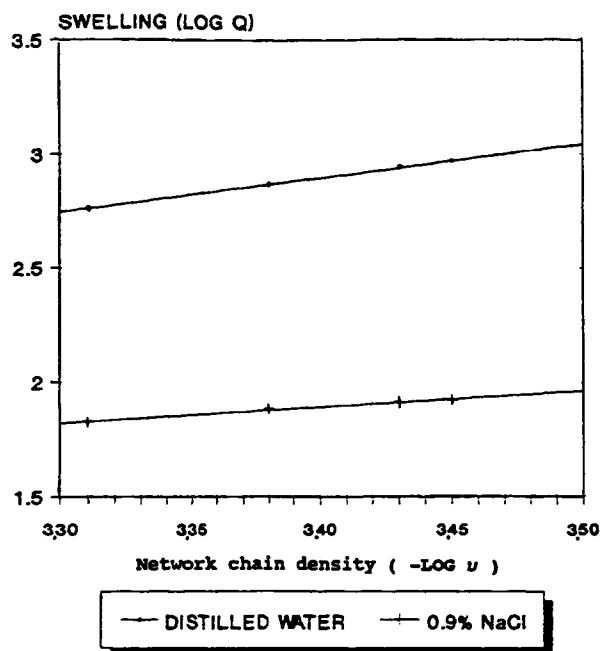**Figure 10**   Variation of swelling with NaCl concentration.

Figure 11 Amount of swelling versus network chain density.

A4 are different in terms of cross-link density. As shown in Figure 7, with a network chain density increase the amount of swelling or degree of swelling decreases. Thus at certain degrees of ionization (neutralization degree) the molar percent of cross-linker to monomer determines the equilibrium water-retaining capacity of the absorbents. Another important parameter is the T_{eq}, that is, the time required to reach equilibrium swelling. It can be seen from Figure 8 that by increasing network chain density this parameter shifts to the lower amounts. In other words by increasing the number of network chains the time needed to absorb equilibrium amounts of water becomes shorter. Figure 9 shows the variation of swelling with changing network chain density in different saline solutions. It can be seen that by increasing the salinity of the solution, the amount of swelling or water uptake becomes in-

dependent of network chain density or cross-link density. The same behaviour is shown in Figure 10: by increasing network chain density the trend of swelling variation becomes smoother. Finally, according to Figure 11, when the logarithmic amounts of swelling is being plotted versus logarithms of network chain density for distilled water and 0.9% NaCl solution, a Power law behaviour is being observed ($Q = (v)^n$). Magnitudes of experimental n exponents for the two above-mentioned solutions are 1.49 and 0.65, respectively.

CONCLUSIONS

By utilizing an inverse suspension polymerization technique on water soluble monomers such as acrylic acid, hydrogels with a high capacity for water retaining can be obtained. For some fields of applications such as agricultural and horticultural use, exact particle size distribution is of minor importance because superabsorbent unmodified systems can be used. But for medical uses such as baby diapers and sanitary napkins some modification of particle size is necessary. This can be performed by the use of macromolecular stabilizers. To obtain superabsorbents with a high capacity of absorption and desirable kinetics, some optimizations chiefly on neutralization degree, amounts of cross-linker used, and monomer concentration must be made.

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