Modifying Acrylic-Based Superabsorbents. II. Modification of Process Nature

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SYNOPSIS

This article is devoted to the synthesis, characterization, and modification of acrylic-based superabsorbents which are synthesized by inverse suspension and solution polymerization techniques. Distilled and saline water absorbency of these hydrogels and the effects of varying process nature on their absorbency characteristics (capacity and rate) are graphically discussed. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The polymerization of acrylic acid or sodium acrylate with a crosslinker in aqueous solution would seem to be a straightforward process. The monomers and crosslinker are dissolved in water at a desired concentration, usually from about 10% to 70%, since polymerization of undiluted acrylic acid is extremely dangerous because of the high heat of polymerization and rapid polymerization kinetics. The monomer solution is deoxygenated by bubbling an inert gas through the solution or by a series of evacuations and repressurizations with an inert gas; then the desired free-radical initiator is added and the temperature brought to the appropriate point to start polymerization. However, using this technique in industrial usage is complicated by a variety of factors.[1] In suspension polymerization, small droplets of aqueous monomer solution are dispersed into a second phase, usually of aromatic or aliphatic hydrocarbons prior to polymerization; free-radical polymerization of the monomer is then conducted in a manner similar to solution polymerization. An obvious reason for using this technique is to simplify handling of the polymerization product. In addition, particle size of the product is more easily defined since it depends in part on the nature and amount of the dispersant or suspension aid used to form the droplets prior to polymerization. However, the process is more complicated; therefore several more ingredients need to be controlled and recycled.[2] In a previous article,[3] a very high rate of absorption and a desirable amount of swelling were highlighted at the expense of the length of time needed for polymerization and economic disadvantages. For this purpose, some trials were made with the solution technique.

EXPERIMENTAL

Table I shows the features of the systems. The samples with C designations in a previous article[3] were taken as inverse suspension-polymerized superabsorbents and samples with B designations were synthesized through the above-mentioned course of synthesis to produce solution-polymerized xerogels. The same course of characterization as in previous articles[3,4] was applied to characterize both types of superabsorbents.

RESULTS AND DISCUSSION

Typical structural properties of these two types of superabsorbents are presented in Table II. Details about deriving structural parameters were reported elsewhere.[5] The samples C1 and B1 have no crosslinking agent and are therefore water soluble. By increasing the salinity of an aqueous solution, the amount of swelling becomes independent of network chain density. This fact is also shown for the su-

Table I Features of the Systems

Features of the Systems	Inverse Suspension	Solution
Monomers	Acrylic acid, acrylamide	Acrylic acid, acrylamide
Neutralizer	Aqueous caustic solution	Aqueous caustic solution
Neutralization degree (%)	75	75
Monomer concentration (%) (based on aqueous phase)	46.5	46.5
Crosslinker type	N, N', methylene Bisacrylamide	N, N', methylene Bisacrylamide
Crosslinker amount (%)	0.0–0.1	0.0–0.1
Initiator type	Potassium persulfate	Potassium persulfate
Initiator concentration (%) (based on monomer)	0.5	0.5
Surfactant type	Span 80	—
Surfactant concentration (%)	0.33	—
Polymerization temperature (°C)	80	80
Polymerization time (min)	90	5
Agitation speed (rpm)	400	400
Continuous phase	Toluene	—

perabsorbents of the B series in Figure 1 and Table III. According to Figure 2, when the logarithmic amounts of swelling are being plotted versus logarithms of network chain density, a "power law" behavior [$Q = (\nu)^n$] is observed for distilled water and 0.9% NaCl solution absorbency. Magnitudes of experimental n exponents for the two above-mentioned solutions are 1.46 and 0.45, respectively.

(Corresponding amounts for the C-type samples are 1.49 and 1.17, respectively.) As clearly shown in Figure 3, water absorbency increases with time in exponential form to equilibrium. By increasing the number of crosslinks, a decreasing equilibrium amount of swelling is observed. Thus, as also seen for other samples, at a certain degree of ionization (i.e., 75%), the molar percent of crosslinker to
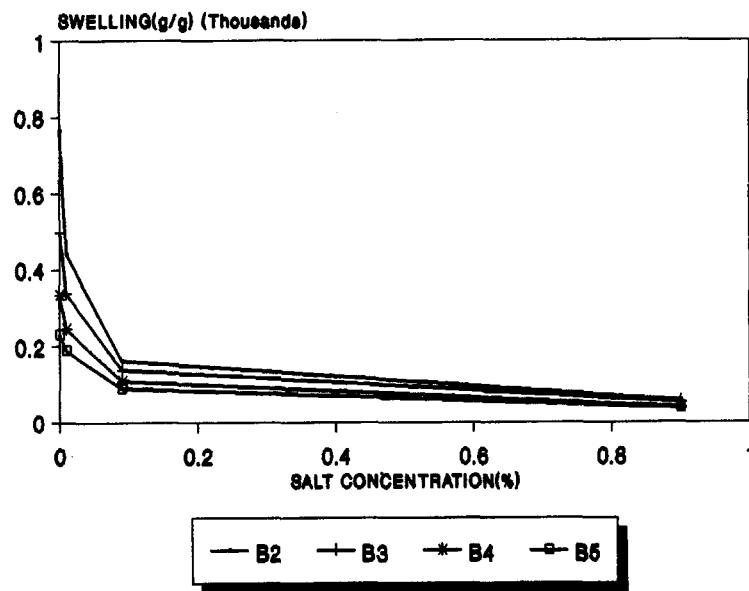

Figure 1 Variation of swelling with NaCl concentration.

Table II Typical Structural Properties of Hydrogels

| Code of Product	C2	C3	C4	C5	B2	B3	B4	B5
Molar % of crosslinker to monomer	1.55×10^{-2}	4.67×10^{-2}	7.79×10^{-2}	0.109	0.775×10^{-2}	1.55×10^{-2}	4.67×10^{-2}	7.79×10^{-2}
Degree of swelling	573.1	422.6	213.1	198.9	765.2	496.8	333.05	230.6
Polymer volume fraction in the gel	1.2019×10^{-3}	1.6292×10^{-3}	3.2258×10^{-3}	3.4591×10^{-3}	9.004×10^{-4}	1.3862×10^{-3}	2.0664×10^{-3}	2.9817×10^{-3}
Crosslink density (mol/cm^3)	6.8892×10^{-5}	8.4572×10^{-5}	1.3418×10^{-4}	1.4068×10^{-4}	5.6716×10^{-5}	7.5844×10^{-5}	9.9308×10^{-5}	1.2722×10^{-4}
Network chain density (mol/cm^3)	1.3778×10^{-4}	1.6914×10^{-4}	2.6836×10^{-4}	2.8136×10^{-4}	1.1343×10^{-4}	1.5168×10^{-4}	1.9861×10^{-4}	2.5444×10^{-4}
Network chain molecular weight	10,524	8,572	5,403	5,153	12,783	9,559	7,300	5,698
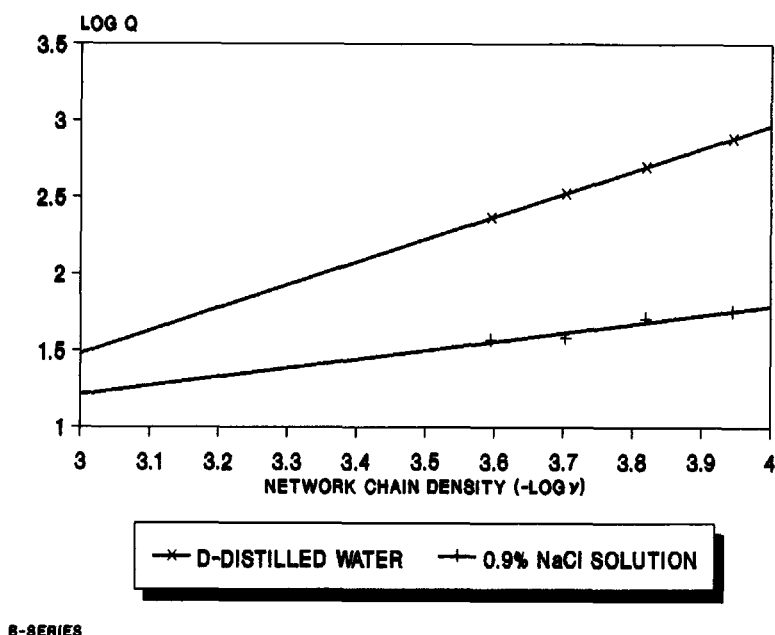
Figure 2 Amount of swelling vs. network chain density.

monomer determines the equilibrium water-retaining capacity of the absorbents. A comparison of the swelling variations for the B and C superabsorbents is shown in Figure 4. As can obviously be seen, the absorption capacities of the B samples are very similar to the C ones, but the rate of absorption for the latter is much higher than for the former. In other words, C superabsorbents can absorb equilibrium amounts of water at a fraction of a minute, but the time for the B samples is considerably longer. Finally, the mechanism of water absorption is affected by network chain density; by increasing the network
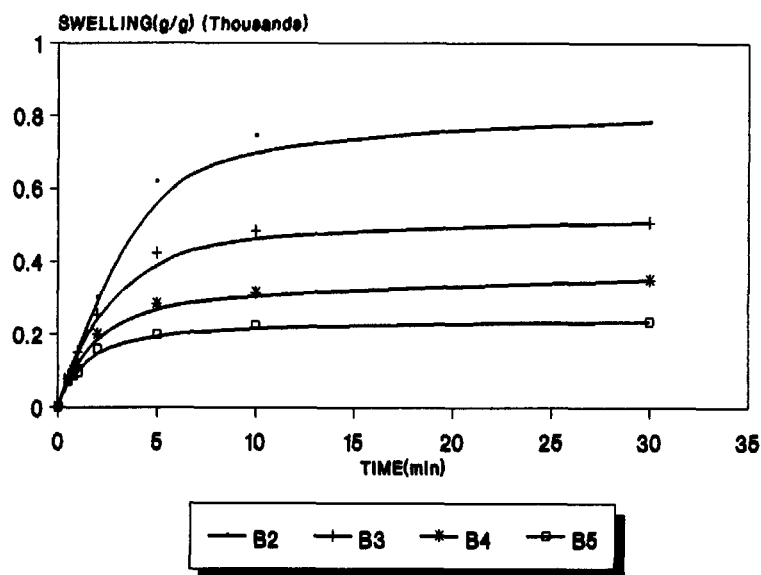
Figure 3 Amount of swelling vs. time for B superabsorbents.
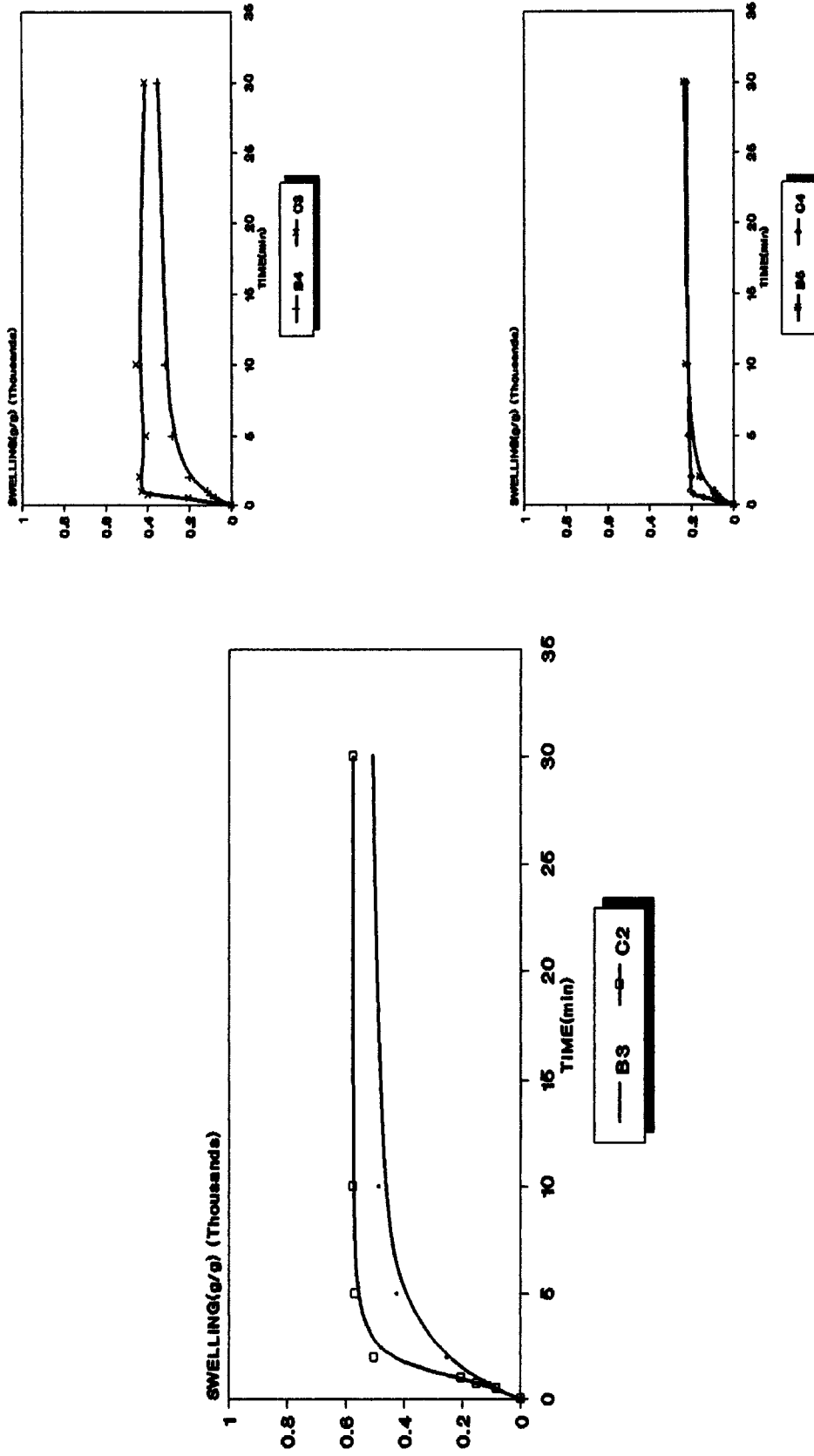
Figure 4 Swelling kinetics for B vs. C superabsorbents.

Table III   Amount of Swelling vs. Salt Concentration

Sample	Amount of Swelling (g/g)			
	B2	B3	B4	B5
Distilled water	765.2	496.8	333.05	230.6
0.009% NaCl	440.8	337.9	245.60	188.8
0.09% NaCl	162.5	138.8	109.70	90.1
0.9% NaCl	56.7	51.6	38.50	37.3

B1 is soluble.

chain density, water transport through superabsorbent becomes diffusion-controlled. Details about the diffusion rate of these superabsorbents will be described in another article.

CONCLUSIONS

Inverse suspension and solution polymerization techniques are satisfactorily applicable to produce superabsorbents with desirable characteristics. When the exact particle-size distribution and a high rate of absorption are needed, the first technique must be utilized. However, to produce a superabsorbing polymer with a high capacity of absorption without the above requirements, a much less expensive, faster technique is recommended.

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