Modifying Acrylic-Based Superabsorbents. I. Modification of Crosslinker and Comonomer Nature

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SYNOPSIS

This article is devoted to the synthesis, characterization, and modification of acrylic-based superabsorbents which are synthesized by carrying out the well-known process of inverse suspension polymerization. The dispersion is stabilized by using a mixture of micromolecular and macromolecular stabilizers. High swelling and appropriate absorption kinetics are obtained, provided that parameters (including initial monomer and crosslinker concentration, range of neutralization degree, initiating and stabilizing system, monomer addition rate, temperature and nature of the organic phase) are being considered. Modifications of crosslinker and comonomer nature and their effects on absorbency characteristics (capacity and rate) of the above-mentioned superabsorbents are graphically presented. Finally, diffusion behavior of superabsorbents is briefly discussed. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Inverse suspension polymerization is defined as a dispersion of a water-soluble monomer(s) in a continuous organic matrix. The latter phase can be either paraffinic or aromatic or the mixture of the two. Thermodynamically, the dispersion is unstable and requires both continuous agitation and the addition of a low hydrophilic–lypophilic-balance (HLB) stabilizer. Initiation is generally carried out chemically with free radical azo or peroxide species and, depending on the desired polymerization mechanism, either of the two is used.[1] However, it is evident that a water-soluble initiator is needed to run inverse suspension polymerization. Inverse suspension is a highly flexible and versatile technique to produce superabsorbents with a high capacity of absorption. As in previous article,[2] it can be seen that superabsorbents crosslinked by oil-soluble crosslinker suffer from the requirement of high crosslinker dosage to show appropriate absorption capacity. Thus, from an economical viewpoint, a modification is necessary. Another disadvantage of these superab-

sorbents (whether or not the modification of crosslinker nature was performed) is the kinetic aspect of absorption, which must be modified for some agricultural or medical applications. Therefore, two types of modifications (modification of crosslinker nature I and modification of comonomer nature II) must be made.

EXPERIMENTAL

Table I shows the features of the base and modified systems. It must be pointed out that modified system I is the base system for modified system II. After numerous orientation experiments and trials based on parameters mentioned in the synopsis, the same courses of synthesis and characterization as in a previous article[2] were applied to synthesize and characterize these types of superabsorbents.

- Process description.
- Dispersed-phase preparation. A predetermined amount of aqueous caustic solution was carefully added (dropwise under cooling) to the acrylic acid to obtain a desired partial neutralization degree.

Table I Features of the Base and Modified Systems

Materials and Conditions	Base System	Modified System I (A series)	Modified System II (C series)
Monomers	Acrylic acid	Acrylic acid	Acrylic acid and acrylamide
Neutralizer	Sodium hydroxide	Sodium hydroxide	Sodium hydroxide
Neutralization degree (%)	75	75	75
Monomer concentration (%) (based on aqueous phase)	46.5	46.5	46.5
Crosslinker type	EGDMA[a]	MBA[c]	MBA
Crosslinker amount (based on monomer) (%)	0.054–4.58	0.0–0.1	0.0–0.1
Initiator type	Potassium persulfate	Potassium persulfate	Potassium persulfate
Initator concentration (%) (based on monomer)	0.5	0.5	0.5
Surfactant type	Span 80[b]	Span 80	Span 80
Surfactant concentration (%) (based on organic phase)	0.33	0.33	0.33
Polymerization temperature (°C)	80	80	80
Polymerization time (min)	90	90	90
Agitation speed (rpm)	400	400	400
Monomer feed rate (g/min)	10	10	10
Continuous phase	Toluene	Toluene	Toluene

[a] EGDMA, ethylene glycol dimethacrylate.
[b] Span 80, sorbitan monooleate.
[c] MBA, N, N', methylene bisacrylamide.

- Continuous-phase preparation. Toluene, the well-known aromatic hydrocarbon, was selected as the organic phase. This matrix containing an appropriate proportion of water in oil (w/o) surfactant was heated to 50°C for 15 min while bubbling nitrogen into the liquid medium. After preparing the two phases and just before running the reaction, defined amounts of a water-soluble crosslinking agent were added to the dispersed phase under nitrogen bubbling until a clear mixture was obtained.

- Polymerization. A four-necked flask fitted with a reflux condenser, a drip funnel, and a thermometer was used. The reactor was heated to 80°C while purging nitrogen; then, at this temperature, the organic phase was added, followed by the dropwise addition of monomer blend while the agitation speed was fixed at a predetermined rate. The reaction mass was left standing for the appropriate time needed to ensure full consumption of the remaining monomers. For all the polymerizations, the monomer feed rate had been set to 10 g/min to allow isothermal polymerization.

Particle size distribution of the samples was found with sieve analysis (using robot sifter). Free swelling was selected to quantify the influence of network chain density on absorbency behavior. One gram of a dry sample was dispersed into 1,500 mL of double-distilled and saline water and allowed to swell sufficiently under mild agitation. After 30 min (that's enough time for all the samples), the dispersion was filtered through a 100-mesh wire gauze and dried carefully using a piece of soft open-cell polyurethane foam until no slipping of the swollen particles at vertical position was observed. The amount of swelling was defined as the weight ratio of the swollen sample to the dry sample.[3] Note that for all the swelling measurements, mesh sizes of 50–60 were examined.

RESULTS AND DISCUSSION

To avoid lump-like beads and to obtain high reasonable rate and capacity, optimized efficiency in retaining fluid and safe processability features, a macromolecular stabilizing system was used.[2] The mean surface diameter of the particles obtained in

this way was about 300 μm. Particle size distribution of the superabsorbents crosslinked by oil-soluble crosslinking agent (EGDMA) was roughly the same as the superabsorbents crosslinked by water-soluble type (MBA). But after oven-drying, it was observed that particles of the latter type were *tightly* adhered to each other while the former particles were *loosely* adhered. Some typical structural properties of these superabsorbents are shown in Table II. Details about deriving structural parameters were reported elsewhere.[3] The sample A1 (with no crosslinking agent) is water-soluble. As clearly shown in Figure 1, by increasing the network chain density (i.e., increasing the amount of the crosslinker used), the amount of equilibrium swelling decreases. Thus, at a certain degree of ionization (i.e., 75%), the molar percent of crosslinker to monomer determines the equilibrium water-retaining capacity of the absorbents. Figure 2 shows the variation of swelling with changing network chain density in different saline solutions. It can be seen that by increasing network chain density, the differences between swellings in different solutions are being reduced. The same behavior is shown in Figure 3. By increasing salt concentration, the amount of swelling corresponding to the various samples with different number of network chains approaches the same point. Consequently, by increasing the salinity of the solution, the amount of swelling becomes independent of network chain density; and by increasing the latter parameter, the trend of swelling variation becomes smoother. This is the same behavior observed for the EGDMA-crosslinked superabsorbents. According to Figure 4, when the logarithmic amounts of swelling are plotted vs. logarithms of network chain density, a "power law" behavior [$Q = (v)^n$] is observed for distilled water and 0.9% NaCl solution absorbency. Magnitudes of experimental n exponents for the two above-mentioned solutions are 1.5 and 0.63, respectively (corresponding amounts for EGDMA-crosslinked superabsorbents are 1.49 and 0.65). Figure 5 reveals the relative efficiency of the two types of crosslinking agents. It is clearly seen that MBA is much more efficient compared to EGDMA (see the slopes). Consequently, from an economical viewpoint, this modification is necessary; but according to Figure 1, kinetics of absorption for these types of absorbents is still poor and must be modified. Experimental evidence showed that by replacing some of the base monomer (acrylic acid) with another comonomer (acrylamide) sol fraction of the absorbent increases and to retain water absorbency and its kinetics in reasonable amount, higher amounts of crosslinker are needed. It was found that optimum results can

Table II Typical Structural Properties of Hydrogels

| Code of Product	A2	A3	A4	A5	C2	C3	C4	C5
Molar percent of crosslinker to monomer	1.55×10^{-2}	4.67×10^{-2}	7.79×10^{-2}	0.109	1.55×10^{-2}	4.67×10^{-2}	7.79×10^{-2}	0.109
Degree of swelling	752.7	516.3	285.4	252.9	573.1	422.6	213.1	198.6
Polymer volume fraction in the gell	8.6195×10^{-4}	1.2561×10^{-3}	2.2700×10^{-3}	2.5610×10^{-3}	1.2019×10^{-3}	1.6292×10^{-3}	3.2258×10^{-3}	3.4591×10^{-3}
Crosslink density (mol/cm³)	1.2529×10^{-4}	1.6145×10^{-4}	2.4068×10^{-4}	2.6112×10^{-4}	6.8892×10^{-5}	8.4572×10^{-5}	1.3418×10^{-4}	1.4068×10^{-4}
Network chain density (mol/cm³)	2.5058×10^{-4}	3.229×10^{-4}	4.8136×10^{-4}	5.2224×10^{-4}	1.3778×10^{-4}	1.6914×10^{-4}	2.6836×10^{-4}	2.8136×10^{-4}
Network chain molecular weight (g/mol)	6,165	4,784	3,209	2,958	10,524	8,572	5,403	5,153
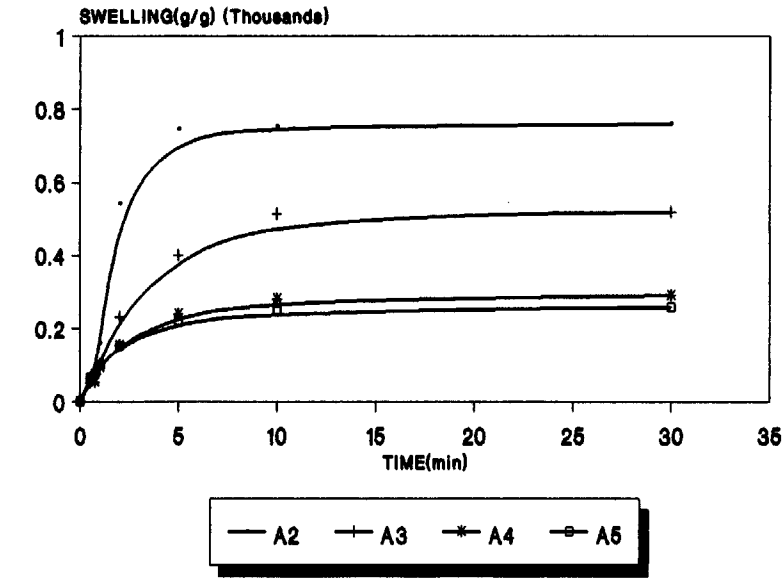
DOUBLE-DISTILLED WATER IS USED
A1 IS SOLUBLE

Figure 1   Amount of swelling vs. time, A series.

be obtained for a 1 : 1 ratio of the two monomers. Regarding to the sieve analysis, the mean surface diameter of the particles obtained was lower than 300 μm (lower than the figure obtained for modified system I). Typical structural properties of these

modified superabsorbents were also reported in Table II. The sample C1 is without a crosslinker and is therefore water soluble. Figures 6 and 7 show the same behavior and results as modified system I. But according to Figure 8, magnitudes of experimental
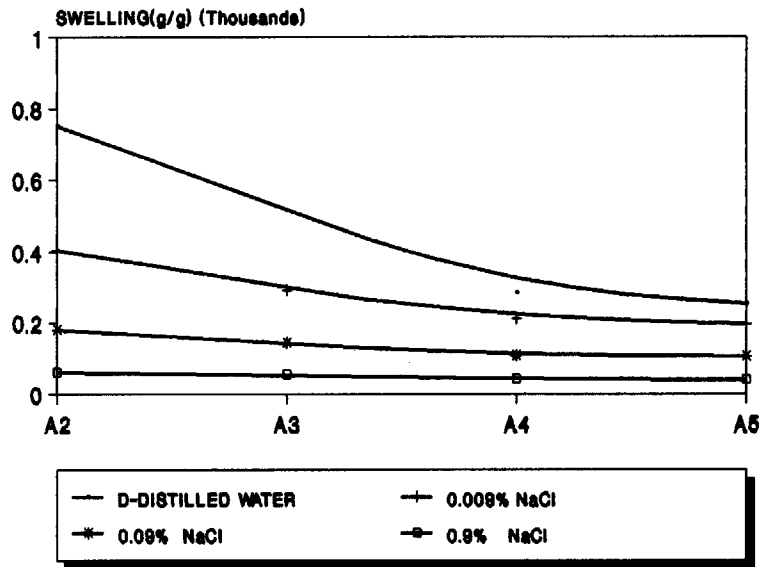
A1 IS SOLUBLE

**Figure 2**   Variation of swelling, A series.
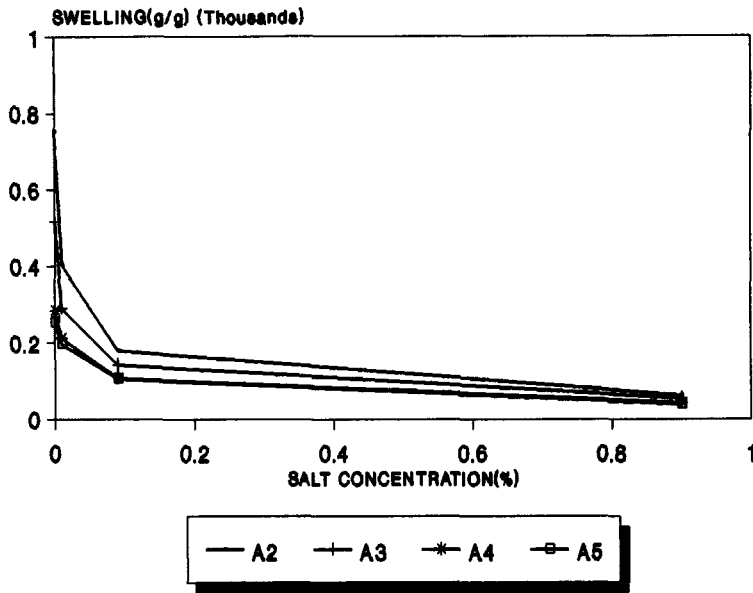
Figure 3   Variation of swelling with NaCl concentration.

n exponents for distilled and saline water absorbency are 1.49 and 1.17, respectively. A comparison of the swelling variation between modified (modified system II) and unmodified (modified system I) superabsorbents is shown in Figure 9. The samples with same numeric indices are similar in terms of the amount of the crosslinker used. As clearly shown, the behavior of the two different samples is very different. Absorption capacity of the unmodified samples is higher than the modified ones (because of the higher amounts of the ions present), but the rate of absorption for the latter is much higher than
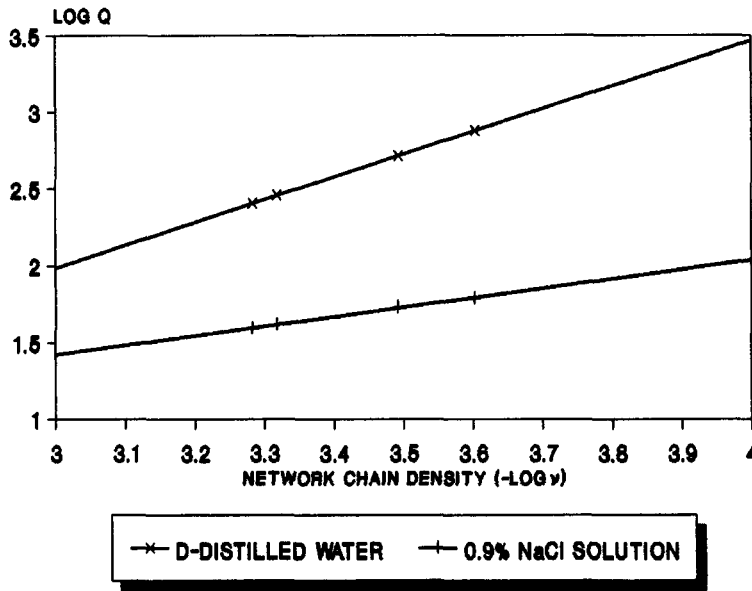
A-SERIES

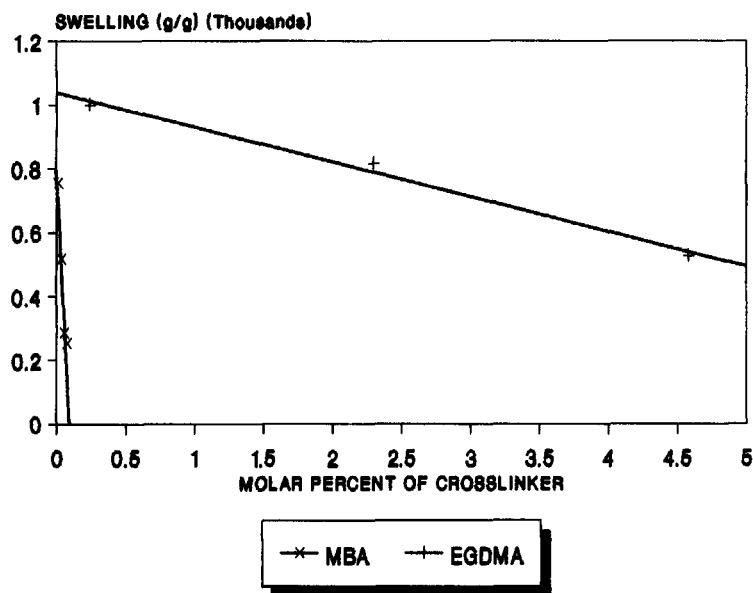**Figure 4**   Amount of swelling vs. network chain density.

Figure 5   Relative efficiency of the two types of crosslinking agents.

for the former. In other words, modified superab-sorbent can absorb equilibrium amounts of water at a fraction of a minute (exactly 30 sec). Finally, it was found for both unmodified and modified samples that when the ratio of time-dependent absorbency (Q_t) to time-independent absorbency or equilibrium swelling (Q_e) is plotted against the square root of time ($T^{1/2}$), by increasing network chain density, this behavior becomes more linear, and at the extreme cases (A5 and C5) becomes completely linear [it is to be noted that this linearity is valid only for limited range of Q_t/Q_e (i.e., between 0.0 and 0.7)].
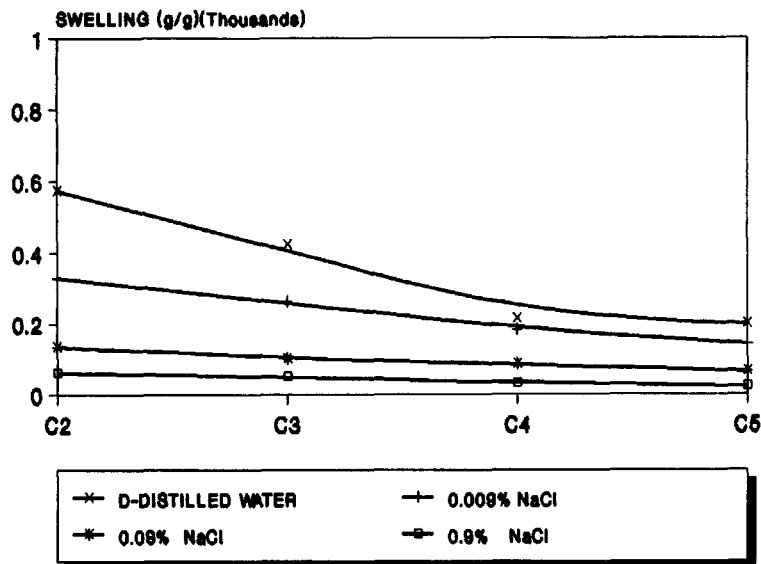
C1 IS SOLUBLE

Figure 6   Variation of swelling, C series.

SWELLING(g/g) (Thousands)

SALT CONCENTRATION(%)
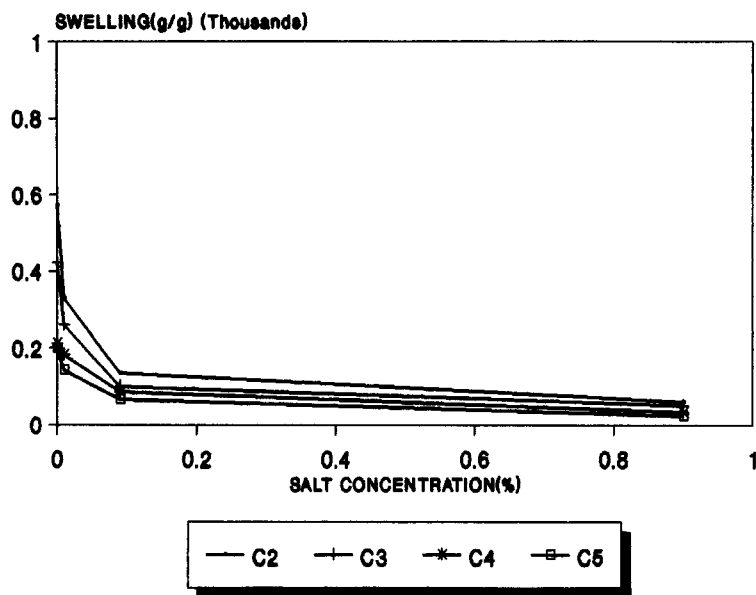
— C2   —+— C3   —*— C4   —□— C5

Figure 7   Variation of swelling with NaCl concentration.

At this point, water transport through the absorbents is diffusion-controlled; and the diffusion coefficient (D) of the samples can be simply computed.[4] Details about the diffusion rate for these superabsorbents will be shown in another article.

CONCLUSIONS

Inverse suspension polymerization is a suitable method for producing superabsorbents with high capacity and rate of absorption from water-soluble

LOG Q

NETWORK CHAIN DENSITY (-LOG v)

—*— D-DISTILLED WATER   —+— 0.9% NaCl SOLUTION
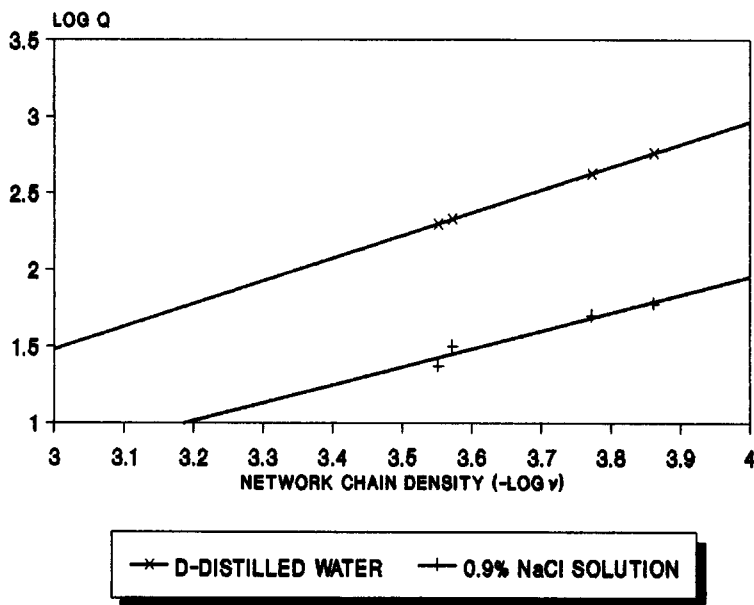
C-SERIES

Figure 8   Amount of swelling vs. network chain density.
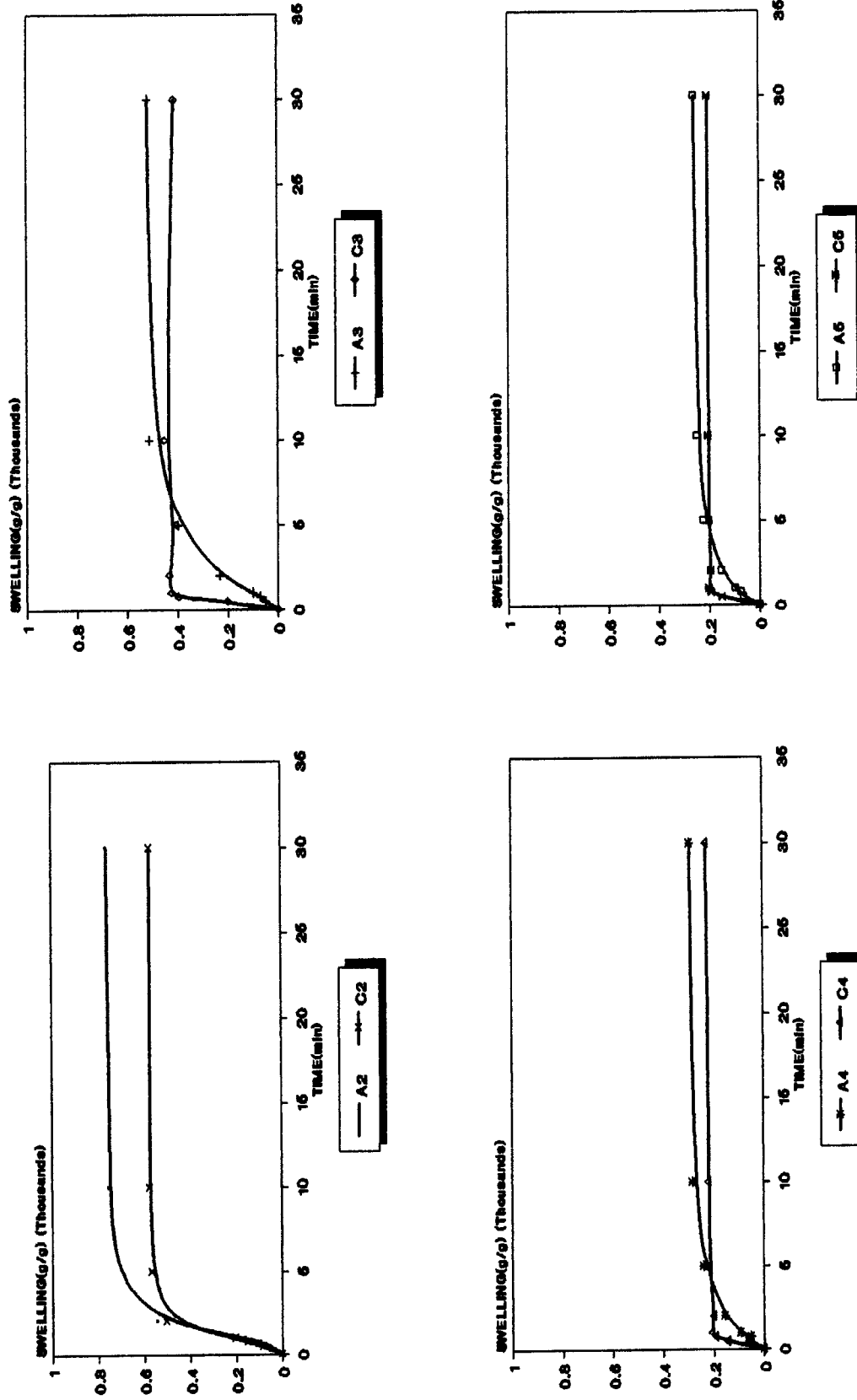
Figure 9   Variation of swelling for modified vs. unmodified superabsorbents.

monomers such as acrylic acid. Regarding the results obtained, the two types of crosslinking agents (EGDMA and MBA) exert similar effects on absorbency behavior in distilled and saline water. Efficiency of the water-soluble one (MBA) is much higher than the oil-soluble type (EGDMA). By replacing some of the base monomer in modified system I with acrylamide, the rate of water absorption progressively increases at the expense of reducing absorption capacity. Absorbency behavior of these modified superabsorbents in distilled and saline water are the same as for unmodified types, but the n exponent of the power law equation for saline water absorbency becomes very different compared to the corresponding amount of n for the unmodified types. Finally, the water absorption mechanism for both superabsorbent systems is dependent on the amount of network chain density or the amount of the crosslinker used.

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4. J. Crank and G. S. Park, *Diffusion in Polymers*, Academic Press, London, 1968.