PII: S0032-3861(97)10236-1

Polymer Vol. 39 No. 15, pp. 3459–3466, 1998
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0032-3861/98/$19.00+0.00

Modified acrylic-based superabsorbent polymers. Effect of temperature and initiator concentration

H. Omidian[a], **S.A. Hashemi**[a,*], **P.G. Sammes**[b] **and I.G. Meldrum**[b]
[a]*Polymer Research Centre of Iran, P.O.BOX 14185/458, Tehran, Iran*
[b]*Department of Chemistry, Brunel University, Uxbridge, Middlesex UB8 3PH, UK*
(Received 8 October 1997; revised 11 November 1997; accepted 3 December 1997)

A solution polymerization process was used industrially to produce superabsorbent polymers based on acrylic monomers. Using a simple, small scale laboratory version of the polymerization part of this process which permits contact with air and evaporative losses, the effects of varying the heat input and the initiator concentration were explored. The presence of oxygen resulted in an inhibition period which lengthened the time for completing polymerization and consequently increased evaporative losses of water. The absorbency of the reaction products was highest under conditions which gave short reaction times. Long reaction times resulted in long inhibition periods, runaway polymerization and low absorbency. These effects were accounted for in terms of oxygen participation in the polymerization and extensive losses of water as the solvent. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: superabsorbents; initiator concentration)

INTRODUCTION

Superabsorbents are hydrophilic crosslinked polymers which can imbibe huge amounts of water[1]. They are used mainly as absorbents in healthcare and agricultural applications and are commonly based on acrylic monomers such as acrylamide, acrylic acid and salts of the acid[2]. The monomers can be polymerized by solution and inverse suspension techniques but the solution method is preferred industrially for economic reasons and for its simplicity. In this process pre-heated solutions of monomers and solutions of crosslinker and initiator are prepared separately, brought together in a nozzle type of mixer, and spread on an endless conveyor belt[3] and allowed to react. The reaction mixture is not agitated in any way, and is open to the atmosphere, providing unrestricted access to oxygen and loss of water vapour.

Although the inverse suspension process facilitates control of temperature, heat transfer and water loss, an earlier exploratory study found that absorbents made by the two polymerization techniques on a small laboratory scale gave similar degrees of ultimate swelling. However the rate of swelling for the suspension process was about 12 times faster[4]. Further studies have found that increasing the amount of crosslinker reduced the ultimate swelling capacity but speeded up the rate of swelling for products made by both processes[5,6].

These exploratory studies have been continued. In the work reported here the dependence of the swelling characteristics on the heat input into the reaction mixture and on the initiator concentration has been investigated for the solution process.

EXPERIMENTAL

Materials

Acrylamide and acrylic acid monomers and methylene bisacrylamide crosslinker were supplied by Merck. Acrylic acid was purified by steam distillation through a column packed with copper gauze to inhibit polymerization. Acrylamide and miethylene bisacrylamide were recrystallized from methanol. The initiator, potassium peroxydisulfate was recrystallized twice from distilled water.

Since the monomer concentrations were the same for each reaction mixture before polymerization, the same procedures for preparing the monomer solutions were used throughout. Separate solutions of acrylamide (3.6 g) and methylene bisacrylamide (0.0012 g) in water (3.214 g and 0.96 g respectively) were prepared. Solutions of potassium persulfate (0.0036–0.144 g) in water (0.96 g) were prepared to give a range of concentrations for one series of runs and a number of solutions at the same concentration (0.08 g) for a series in which the temperature was varied. Acrylic acid (3.6 g in 1.8 g water) was partially neutralized (75% mol/mol) by pH titration to the sodium salt with a solution of sodium hydroxide (1.5 g) in water (4.35 g). Owing to the limited solubility of methylene bisacrylamide in concentrated monomer solutions it was added first to the acrylamide solution. Once the monomer solutions were combined their molar ratios were 1/3/4 for acrylic acid/sodium acrylate/acrylamide. The initiator solution was added to the combined monomer solutions immediately before starting the reaction.

Polymerization procedure

The reaction mixture (20 g) was poured into a beaker (400 ml) fitted with a digital thermocouple to monitor the reaction temperature and a magnetic stirrer. The beaker was

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[*] To whom correspondence should be addressed

immersed in a thermostatic oil bath at a temperature which was in the range 75–180°C for the series of runs in which the temperature was varied and 120°C for the series in which the initiator concentration was varied. Stirring was continued until the reaction mixture became too viscous and gelled. The gel point was taken to be the time at which bubbles no longer escaped and the stirrer stopped. The beaker was then removed from the bath and allowed to cool to room temperature. The reaction product was removed and cut into small pieces (2–5 mm) which were dried overnight in an air-circulating oven at 60°C to constant weight. The dried product was powdered with a hammer-type mini-grinder and screened using an automatic sieve. The classified particles were stored in stoppered bottles.

Swelling measurements

For dried polymers a fixed amount (0.2 g ± 0.001 g) of classified (250–300 μm) product was dispersed in 400 ml of doubly distilled water and allowed to swell with mild agitation for different times. Each dispersion was filtered through a 100-mesh wire gauze and surface water was removed carefully from the retained gel using a piece of a soft, open-cell polyurethane foam. The drying process was found to be complete when the gel particles no longer slipped from the gauze when it was held vertically. The degree of swelling was determined from the weight gain on the gauze after immersion in water per unit weight of absorbent before immersion. Three different samples were examined for each time of swelling and averaged. The standard deviation was found to be ± 2.1 g. The sampling procedure was repeated until the degree of absorption became constant. For undried products the same procedure was followed, except that 1 g quantities of bulk material were used instead of 0.2 g of classified product and immersed into 2 l of double distilled water. Swelling measurements were made without extraction by water.

Water extraction

Dried reaction products were extracted with water to determine how much was not bound to the polymer network. Each product (0.5 g) was immersed in a large excess (500 ml) of sodium chloride solution (1% wt/wt) and shaken at intervals over a 72 h period. The presence of the salt restricted the amount of swelling and improved the accuracy by using more superabsorbent per unit volume of extracting medium. A known weight of supernatant liquid was heated in an air-circulating oven at 90°C to dryness, and weighed to give the total amount of solute extracted.

Table 1 Absorption characteristics and extractables at the gel point for different bath temperatures and same initiator to monomer mol% ratio of 0.295

Run no.	Bath temp (°C)	Gel time (s)	Wt% water in undried product	Equilibrium swelling of undried product (g/g)	Equilibrium swelling of undried product without water (g/g)	Equilibrium swelling of dried product (g/g)	Wt% water extractables in dried product
1	75	1094	1.1	267	269	331	–
2	90	720	4.2	296	309	355	22
3	97	500	16	270	322	319	–
4	105	345	23.5	325	423	340	12
5	112	200	34	505	765	420	–
6	120	128	38	615	994	588	14
7	127	108	37	615	980	569	–
8	135	88	37	593	942	686	6.5
9	142	74	37.5	650	1041	838	–
10	150	63	37	722	1142	848	9.8
11	157	56	37	622	985	826	–
12	165	48	37	641	1012	877	7.2
13	172	46	35.5	655	1015	827	–
14	180	42	35.5	621	961	833	–

Table 2 Absorption characteristics and extractables at the gel point for different ratios of initiator to monomer, [I]/[M], and a bath temperature of 120°C

Run no.	[I]/[M] moles) × 100	Gel time (s)	Wt% water in undried product	Equilibrium swelling of undried product (g/g)	Equilibrium swelling of undried product without water (g/g)	Equilibrium swelling of dried product (g/g)	Wt% water extractables in dried product
15	0.010	709	0.12	276	275	609.2	25.13
16	0.021	500	11.8	390	441	561.15	14.50
17	0.044	187	11.3	448	503	750.44	10.13
18	0.087	203	33.3	674	1008	749.81	3.63
19	0.176	122	37.2	642	1020	720.96	4.25
20	0.264	110	39.5	549	905	750.13	–
21	0.325	106	38.4	750	1215	808.33	6.13
22	0.441	94	39.7	926	1533	943.01	2.38
23	0.529	92	39.9	939	1562	930.22	–

Table 3 Changes in concentration resulting from evaporative losses of water at different bath temperatures

Temperature (°C)	75	105	120	142	165	180
Wt% water lost after reaction	98	60	35	38	39	41
Wt% water lost from aqueous solution without reaction	86	24	9	7	5	6
Wt% water loss due to reaction	13	36	26	31	33	35
Water lost before reaction/ water lost during reaction	7	0.67	0.35	0.22	0.16	0.18
Wt% monomers in reaction mixture at gel point	83	47	42	42	41	41

Table 4 Changes in concentration resulting from evaporative losses of water at different initiator concentrations

[I]/[M] × 100 (mol)	0.01	0.021	0.044	0.087	0.176	0.264	0.325	0.441	0.529
Wt% of original water lost after reaction	99.8	80	81	44.5	38	34	36	33.8	33.5
Wt% of original water lost at gel time without reaction	50.7	28.8	10.8	6.4	3.3	2.6	2.7	2.2	2.2
Wt% of original water lost during reaction	49.1	51.2	70.5	38.1	34.7	31.4	33.3	31.6	31.3
Water lost before reaction/water lost during reaction	1.03	0.56	0.15	0.16	0.09	0.08	0.08	0.07	0.07
Wt% monomers in reaction mixture at gel point	69	48	42	41	41	40	40	40	40

RESULTS

Gel times ranged from 1094 s to 42 s as the bath temperature was raised from 75°C to 180°C, as shown in *Table 1* and from 709 s to 92 s as the initiator concentration was raised from 0.01 to 0.529 mol% ratio on monomer as shown in *Table 2*.

In each case there was an initial period when the temperature of the reaction mixture rapidly rose from ambient temperature towards the bath temperature. However the reaction mixture only reached the bath temperature at the low end of the range. The highest temperature observed was 110°C. At the longer gel times reaction only became apparent near the end of the period. For example at a bath temperature of 75°C nothing appeared to happen for the first 18 min, and then a vigorous reaction suddenly occurred within seconds, resulting in the stirrer slowing down and stopping as the viscosity increased and in foaming as the temperature rose to nearly 110°C. On cooling to room temperature the reaction mixture was found to have been transformed to a glassy, white and porous state. At high bath temperatures and short gel times the reaction was much less vigorous, resulting in less foaming and in the final product being a soft, transparent and rubbery material. This was the case for bath temperatures in the range 120–180°C.

Before reaction the concentration of water in each reaction mixture for both series of reactions was 60 wt%. As shown in *Table 1* the water contents in the reaction mixtures for the series of reactions at different temperatures dropped to 34–38% after reaction for bath temperatures from 112–180°C, but dropped much more at lower bath temperatures and fell to just 1% at the lowest. These contents correspond to losses of water ranging from 43–41 wt% of the water originally present at the upper temperatures to 98 wt% at the lowest temperature. A similar pattern of water loss is evident in *Table 2* for the series of reactions at different initiator concentrations. At initiator to monomer ratios from 0.00529 to 0.00087 the water content dropped to 33–40 wt%, but at lower concentrations the water content dropped as far as 0.12 wt%.

Separate experiments were carried out to measure rates of evaporation of water caused solely by the heat from the bath., i.e. in the absence of any reaction. For each bath temperature and each initiator concentration in *Tables 1 and 2* the loss in weight due to evaporation was measured for the same amount of aqueous solution as used in the reaction mixture. These losses in weight, expressed as percentages of the original water present, are compared with the losses from the reaction mixtures in the temperature series in *Table 3* and with the losses from the initiator series in *Table 4*.

In *Table 3* the evaporative losses from the aqueous solutions before reaction are in the range 5.4–9.1 wt% of the water originally present for bath temperatures from 180 to 120°C. They increase to 24.1 wt% at 105°C and reach 85.5 wt% at 75°C. The difference between the losses after reaction and the losses without reaction gives the losses due to reaction, which are in the range 26–36 wt% at temperatures of 105–180°C and drop sharply to 13 wt% at 75°C. The ratio of the water lost before reaction to the water lost during reaction decreased rapidly as the bath temperature was raised from 75°C and appears to have levelled off at about 0.18 at higher temperatures. At 75°C the monomer concentration just before reaction increased to 83 wt% from the original value of 40 wt% because of water evaporation but at higher temperatures was almost unchanged. The increasing importance of the water loss before reaction with decreasing bath temperature is shown more strikingly in *Table 3* by the change in ratio of water lost before reaction to the loss during reaction from the lowest value of 0.16 to the highest value of 7.

In the same way the variation of water loss with initiator concentration is shown in *Table 4*. As the initiator concentration was increased from 0.01 to 0.525 mol% the loss in water after reaction, expressed as the proportion of the water originally present, dropped from 99.8% to a steady value of about 34%, and similarly the amount of water lost before reaction dropped from 50.7% to a steady value of about 2.5%. The difference gave the amount of water lost during the reaction, and apart from a high value of 70.5% this ranged from about 50% to 32%. The ratio of the water lost before reaction to the water lost during reaction decreased from 1.03 at the lowest initiator concentration to a steady value of about 0.07 at the highest concentrations. The monomer concentration just before reaction was a little more than the original value of 13 mol% at higher initiator concentrations and rose to 23 mol% at the lowest concentration.

The swelling characteristics of reaction products for bath temperatures ranging from 75 to 180°C are given in *Table 1*. Amounts of swelling for both undried and dried products increased with temperature but levelled off at about 140°C. The amounts of swelling by the undried products are smaller than for the dried products at temperatures ranging from 135°C to 180°C and from 75°C to 97°C, but at temperatures in the range 105–127°C the swelling by the undried products is similar to, or even higher than the swelling by the dried product. When allowance is made for the water contents in the undried products then the amount of swelling per unit mass of neat product becomes considerably higher for the undried product than for the dried product over the temperature range 105–180°C, but is still lower for the undried product at 75°C and 90°C.

Similarly the swelling characteristics of undried and dried reaction products for initiator/monomer ratios of 0.01/0.529 mol% and at a bath temperature of 120°C are listed in *Table 2*. The amounts of swelling for dried product increased with increasing initiator concentration and ranged from 561 to 930 g/g. These values are higher than for the series of runs at different temperatures. Experiment 6 in *Table 1* can be compared with the experiment which should be somewhere between Experiments 20 and 21 in *Table 2*. With nearly the same gel time and amount of water in undried product, the amount of swelling is higher for the latter. Although swelling for undried product at the highest initiator concentration is the same as for dried product, at the lowest concentration it is less than half. On allowing for the water content in the undried product as before, the highest amount of swelling for undried product, 1562 g/g, became considerably higher than for dried product whereas the lowest amount of swelling was still less than half.

DISCUSSION

Reaction kinetics

The experimental observation that the gel time was inversely proportional to the square root of the persulfate initiator concentration (*Figure 1*) is as would be expected for a normal polymerization[7]. However, the polymerization was not normal. There was no attempt to exclude oxygen, and there was an inhibition period which became longer as the persulfate concentration was reduced. Precipitation of the reaction mixture in nonsolvent during this period showed that only small amounts of polymer were produced and there was no sign of an increase in viscosity. The existence of an inhibition period in the presence of oxygen is well established for free radical polymerizations in general[8] and for acrylic monomers in particular[9]. Studies carried out by Barnes and others[10–12] have shown that oxygen essentially forms an alternating copolymer with the monomer, i.e. a polyperoxide (–M–O–O–). Moreover the rate of addition of monomer to the peroxide radical formed by addition of oxygen to the polymer chain could be as slow as one thousandth of the normal rate of polymerization. As described by Flory[8], the inhibition period is brought to an end by faster than normal polymerization as a result of the polyperoxide decomposing and yielding initiator radicals.

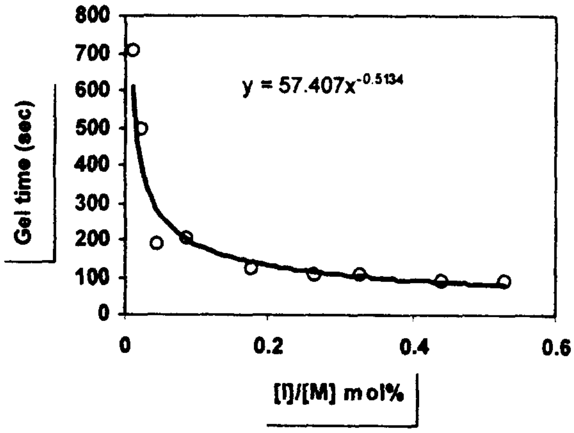

Figure 1 Exponential relationship between gel time and initiator concentration

If the polymerizations reported here proceeded in this manner then a possible reaction scheme can be formulated as follows:

(i) $K_2S_2O_8 \rightarrow 2OH^*$	Initiator radicals
(ii) $OH^* + M \rightarrow M^*$	Monomer radical
(iii) $M^* + M \rightarrow M^*$	Normal polymer radical
(iv) $M^* + O_2 \rightarrow O_2^*$	Peroxy radical
(v) $O_2^* + M \rightarrow M^*$	Polyperoxide radical
(vi) $2PP^* \rightarrow PP$	Recombination of polyperoxide radicals

The first step is as usual taken to be the decomposition of persulfate initiator (i), leading to the production of a pair of OH* radicals[13]. Polymerization is then initiated by addition of these radicals to monomer and normal propagation would consist of addition of further monomer units (iii). During the inhibition period oxygen adds on to the monomer radical forming a peroxy radical. Addition of monomer to the peroxy radical is much slower than to the normal polymer radical, resulting in suppression of the normal propagation reaction and formation instead of a polyperoxide chain alternating in end group between monomer and peroxy radicals. Usually termination is attributed to combination or disproportionation of the polymer radicals. In this case the reaction is complicated by the two end groups for the polyperoxide, PP*, but would still be bimolecular.

If, as usual, the rate of initiation is assumed to be the same as the rate of termination for steady-state conditions, then the rate of production of polyperoxide in terms of number of moles of monomer segments is given by an expression with a square-root dependence on the concentration of initiator[14].

$$R_p = k_{iv}(ek_i[K_2S_2O_8]/k_v)^{1/2}[M]$$

In this expression the subscripts of the rate constants, k, correspond to reactions in the above scheme, and e is the efficiency of conversion of persulfate into active radicals. The addition of monomer to the peroxy radical is taken to be the rate controlling step in the propagation reaction.

According to this reaction scheme the polyperoxide would accumulate at a rate inversely proportional to the square root of the persulfate concentration. The degree of polymerization is reported by Flory[8] to be low, in the range 10–40. Nevertheless each peroxide link might be a potential source of free radicals for initiating polymerization. If so

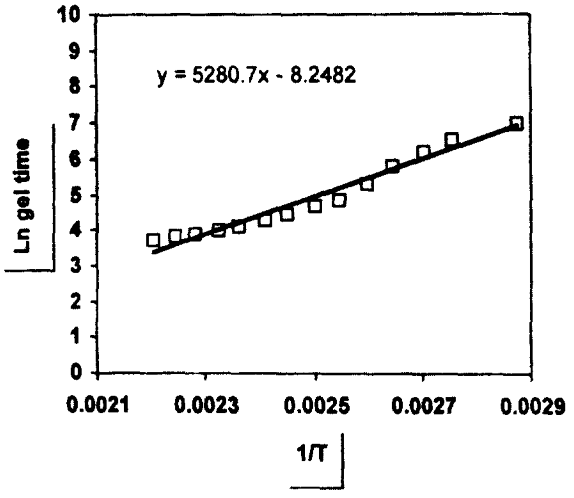

Figure 2 Logarithmic relationship between gel time and absolute temperature (K)

then the concentration of initiating radicals would increase with time, leading to more polyperoxide and to a self accelerating process. At some point the concentration of initiating radicals might become high enough to enable significant amounts of normal polymerization to occur, resulting in a rapid increase in viscosity, slowing of oxygen diffusion and rise in temperature.

Figure 2 shows an Arrhenius plot of gel time against bath temperature. This would not be expected to fit the data accurately, because the reaction temperature was not necessarily the same as the bath temperature, but the data give a fair approximation to the following relationship:

$$\text{Ln}R_p = -8.2482 + 5280/T$$

and reducing the temperatures for runs at the upper end of the range would improve the linearity of the plot.

Effects of changes in water content before and after reaction

A complicating factor in the polymerization process was the loss of water by evaporation. It is known that when the concentration of acrylic monomers exceeds a certain level[15] that runaway polymerization occurs. However this has presumably been observed for normal polymerization, and is attributable to reduced heat transfer. A mechanism would still be required to account for oxygen inhibition being overwhelmed by normal polymerization, despite free access to oxygen. Although the possibility cannot be excluded that the inhibition period ended as a result of water loss, polyperoxide is known to form under the conditions of polymerization used here, and it seems more likely to provide an explanation for the observed increase in reaction vigour with decreasing initiator concentration and decreasing temperature as a result of the accumulation of peroxide.

For both the temperature and initiator series of runs the water contents in the reaction products at the longest reaction times were so low ($<$ 10 wt%) that they became glassy. This suggests the possibility that polymerization was brought to a stop prematurely by lack of monomer mobility whereas polymerizations which lost less water stayed in a rubbery state and were able to continue polymerizing to a higher degree of conversion, resulting in higher degrees of swelling. If so, then some correlation might be expected between the water contents of the products and their degrees of swelling. For the series of runs in which the temperature was varied the water contents of the reaction product were nearly constant over the range 180–120°C and the degrees of swelling for the undried products were nearly constant too, apart from a high value at 150°C. Although the degrees of swelling for dried products were also nearly constant over much of the range for dried products, they became smaller at temperatures below 142°C. Most of the data for the temperature series therefore appear to be consistent with the degree of conversion of monomer to polymer depending on the water content in the reaction product.

The estimates of evaporative losses in *Table 3* show that the amount of water in the reaction mixture at the gel point for bath temperatures of 120°C or more was only a little lower than it was before immersion in the bath, because the reaction time was short. However as the bath temperature was reduced below 120°C the reaction time became longer and at 75°C the evaporative losses became so large that only 14 wt% of the water originally present remained at the onset of rapid polymerization. This can be expected to have affected the polymerization considerably. It is reported[15] that acrylic acid undergoes runaway polymerization when the monomer concentration is about 0.3–0.4 mol fraction. As shown in *Table 3*, the monomer concentration at the gel point is estimated to have been close to 40 wt% at bath temperatures of 120°C or more, but to have exceeded this at lower temperatures, reaching 86 wt% at 75°C. Runaway polymerizations could therefore be expected at bath temperatures below 120°C, and this seems to be consistent with experimental observations of smooth polymerization at bath temperatures above 120°C and noise-emitting polymerization at lower temperatures. The low level of water remaining at the onset of rapid polymerization when the bath temperature was 75°C also suggests that conversion of monomer to polymer might be restricted by lack of water, as suggested by the lower degree of absorption than for higher bath temperatures.

For the series in which the initiator concentration was varied the water content in the reaction product was nearly constant over the initiator: monomer ratios in the range 0.00529 to 0.00176 but the degree of swelling for both undried and dried products became smaller. Evidently the degree of swelling was affected by other factors. If the degree of swelling depended solely on the degree of conversion of monomer to polymer then conversion at the lowest initiator concentration may have been less than one third of conversion at the highest concentration. Although the fifty-fold difference in initiator concentration is more than large enough to influence conversion to this extent, other factors may have been influential as well.

Conversion in the final product depended not only on when the mixture was removed from the bath but also on how much further conversion progressed as the mixture cooled. For products in a rubbery state conversion may have increased considerably. Comparison of the highest degrees of swelling (926, 939 g/g) with those obtained previously for polymerizations where the degree of conversion was known to be nearly complete[16] indicates that conversion must have been high for Runs 22 and 23 at the highest initiator concentrations. Given that the reaction mixture temperatures at the gel point did not exceed 110°C, and assuming that reaction stopped when the temperature dropped to a level at which initiator decomposition became too low to maintain propagation, then it follows that the degree of conversion beyond the gel point depended on the rate of polymerization at the gel point. For runs at the upper end of the initiator concentration range this additional conversion will have become smaller with decreasing concentration. For runs at the lower end of the range there was an increase in the rate of reaction at the gel point, which has been attributed to the formation of polyperoxide, but this was accompanied by loss of water. The resulting transformation from a rubbery gel to a rigid glass accounts for the failure of the acceleration in reaction to yield a high conversion.

Another feature of the results for the initiator series is the difference in the effect of drying the product on swelling at the two ends of the initiator concentration range. Whereas swelling was more than doubled at the low end, it was unchanged at the high end. Since the drying procedure involved heating the sample at 60°C for 24 h, the increase in swelling could be accounted for by resumption of polymerization and increased conversion. This explanation is consistent with the substantial increases in swelling being restricted to the three products with low enough water contents to be glassy. At the upper end of the initiator concentration range the swelling of dried product might have been expected to exceed the value for undried product because of the higher active content in the dried product, whereas the two values are the same and the swelling calculated for the active part of the undried product is higher by two thirds than for the dried product. It would therefore appear that drying reduced swelling by active product at high initiator concentrations, presumably by causing cross-linking. Although the swelling (549 g/g) for undried product, Run 20, was lower than expected from the data for neighbouring runs, the swelling for dried product (750 g/g) was in line with its neighbours, suggesting that the former value was in error.

Similar effects occurred in the temperature series, but less markedly. Instead of the swelling of dried product being twice that for neat, undried product at the longest gel time, it only increased by 23%, and instead of swelling increasing by 67% at the longest gel time it only increased by 34%. Although the highest bath temperature (180°C) was well above the bath temperature in the initiator series (120°C), there was much less difference in the reaction temperatures, and the initiator ratio (0.00295) was well below the highest ratio in the initiator series. Under these conditions the rate of polymerization at the gel point would have been slower and so less conversion of monomer to polymer could be expected in the final product. This deduction is consistent with the observed lower degrees of swelling for the temperature series. At the lowest bath temperature (75°C) the degree of swelling by the dried product (267 g/g) was close to that (276 g/g) for the lowest initiator concentration, suggesting that the degree of conversion of monomer to polymer was similar. This is supported by the similar amounts of extractables in *Table 1* for Run 2 (22 wt%) and in *Table 2* for Run 15 (25 wt%).

Just as the evaporative losses at the onset of fast polymerization for the temperature series were low for high bath temperatures, so were they also low for the higher initiator concentrations which gave short reaction times. At initiator concentrations from 0.529 to 0.044 mol% of the reaction mixture the evaporative losses were low enough (<11 wt%) to expect little influence on the reaction at the gel point, but at lower concentrations the losses became significant although they did not reach as low a level as for the temperature series, because the reaction time was not as long. Consequently the smallest proportion of water remaining at the onset of rapid polymerization (49 wt%) was substantially higher than for the temperature series (14 wt%). Nevertheless, nearly all of the remaining water was lost during polymerization. As for the temperature series the monomer concentration at the onset of rapid polymerization was close to 40 wt% for most of the reactions, but was higher than this for the two longest gel times. Again these were the reactions which showed characteristics of runaway polymerizations and became glassy.

Application of Voigt model to rates of swelling

Rates of swelling for the absorbents in the temperature and initiator series were found to fit the same Voigt expression (*Figures 3 and 4*) as previously[17]. This expression relates the degree of swelling, ε, to the time taken, t, using two parameters, one representing the resistance of the absorbent to expansion, σ_0/E, and the other representing the resistance to permeation, τ_0, as follows:

$$\varepsilon(t) = \sigma_0/E[1 - \exp(t_0 - t)/\tau_0]$$

Values for these parameters are given in *Table 5* for the dried products. The effect of increasing the temperature and the initiator concentration was to increase both parameters, indicating that both the resistance to expansion and the resistance to permeation were becoming greater. These trends are consistent with increasing conversion of

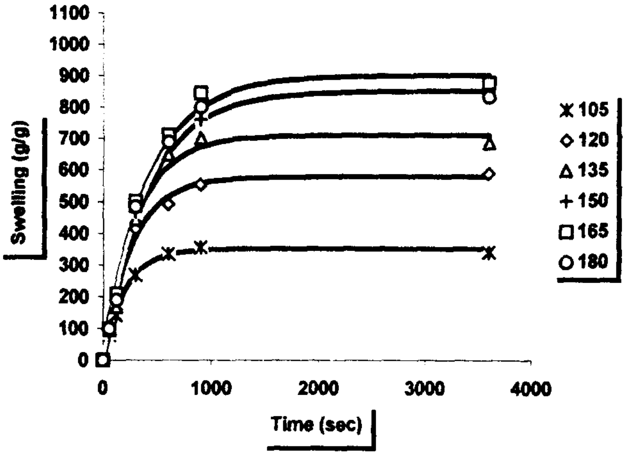

Figure 3 Experimental and modelled dynamic swelling figures for the materials obtained at different temperatures (°C)

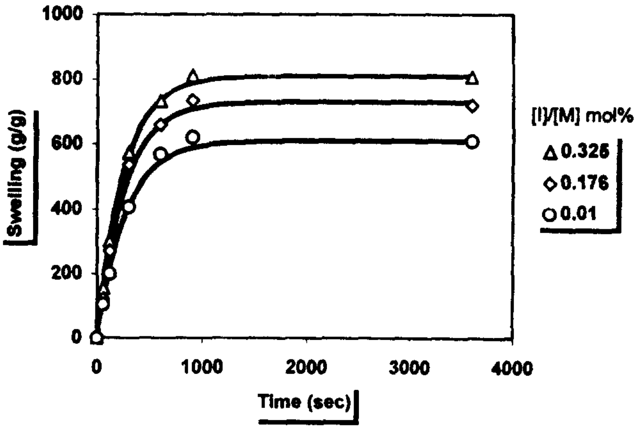

Figure 4 Experimental and modelled dynamic swelling figures for the materials obtained at different initiator loadings

Table 5 (a) Model parameters for temperature variable system. (b) Model parameters for initiator variable system

(a)

Run no.	2	4	6	8	10	12	14
Temperature (°C)	90	105	120	135	150	165	180
σ_0/E (g/g)	355	351	578	710	850	900	870
τ_0 (s)	159	203	269	305	410	415	405

(b)

Run no.	19	20	21	22	23
[I]/[M] (mol%)	0.176	0.264	0.325	0.441	0.529
σ_0/E (g/g)	730	730	810	960	950
τ_0 (s)	258	258	250	350	340

monomer to polymer, since monomer would rapidly diffuse from the absorbent, speeding up absorption, and would contribute little to resistance to expansion. More directly the data in *Tables 1, and 3* for extractables from the products provide evidence for significantly lower conversion of monomer to polymer at low bath temperatures and low initiator concentrations.

It should be noted that, based on the numerous experimental swelling data we have found throughout this work, followed by fitting them into an appropriate mathematical relationships, i.e. Voigt model expression, the standard deviation of the model was found about ± 2.7 g of water/g of dry superabsorbent.

CONCLUSIONS

Preliminary laboratory investigations of the solution process which is used industrially for producing superabsorbent polymers have shown that unrestricted access of the reaction mixture to oxygen and unrestricted evaporative loss of water complicated the polymerization of the acrylic monomers and the swelling characteristics of the products. The existence of an inhibition period, especially at long reaction times, was attributed to the formation of peroxy radicals with low reactivity, as has been established in the past for similar monomer systems. The ending of the inhibition period with the onset of rapid, apparently normal polymerization is thought to result from the accumulation of polyperoxide which eventually yields enough active free radicals to overwhelm the inhibiting effect of the oxygen and set off a self accelerating process in which the heat released by normal polymerization increases the rates of peroxide and initiator decomposition and the rise in viscosity restricts the inward flow of oxygen and outward flow of heat.

The delay caused by the inhibition period provided more time for water to be lost by evaporation, and at lower temperatures and initiator concentrations the losses became large enough to raise the concentration of monomer into the range where runaway polymerization has been reported for acrylic monomers, even in the absence of polyperoxide. Both effects may have combined to induce runaway polymerizations at long reaction times.

The highest degrees of swelling for reaction product were obtained at the higher temperatures (140–180°C) and higher initiator concentrations (0.004–0.005 mol/mol of monomer) in the ranges covered. Substantial reductions in swelling with decreasing temperature or initiator concentration is attributed to two factors. One is the shortening of kinetic chain lengths as initiation by the polyperoxide became more important. The other is the loss of mobility when the remaining water level became so low at long reaction times that the product changed from a rubbery state to a glassy one. The resulting restriction in molecular mobility is believed to have limited the conversion of monomer to polymer, and to have altered the swelling characteristics of the product. Drying the products by heating for a day at 60°C had two effects. One was to reduce the swelling at short gel times compared with neat, undried product. This was attributed to crosslinking. The other effect was to increase the swelling at long gel times. This correlated with quantities of water extractables from dried products and is attributed to further conversion of monomer to polymer. Applying the Voigt expression to the time dependence of swelling provided further support for attributing decreases in swelling at lower temperatures and initiator concentrations to less conversion of monomer to polymer.

Overall it is clear that the highest degrees of swelling for products made by the solution process without restricting access to oxygen and evaporation are obtained when the reaction conditions such as temperature and initiator concentration favour a short reaction time. Further studies would be needed to check the explanations offered for the various effects of oxygen and evaporation. Usually precautions are taken to avoid these effects in studies of free radical polymerizations, and they do not appear to be featured in publications on the subject, even though they might be important in applications such as coatings, adhesives and resin based products, where polymerization occurs in the presence of air. If similar effects occur in these applications as has been observed here, then properties are likely to be downrated, particularly at surfaces.

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