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KINETICS OF POLYMERISATION OF PARTIALLY NEUTRALISED ACRYLIC ACID IN INVERSE SUSPENSIONS

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SUMMARY: The inverse suspension of partially neutralised acrylic acid was investigated and it was shown that variations of initiator and surfactant concentrations had little effect on the rate of reaction, but that a minimum initiator concentration and maximum stirring rate existed. The apparent activation energy was found to be very high with respect to literature values.

Introduction

Partially-neutralised acrylic acid polymers are often used as superabsorbant polymers (SAPs). Generally speaking, they are polymers with a low degree of reticulation, and despite being able to absorb hundreds or thousands time their own weight in water, are nevertheless not hydrosoluble. It is this property of absorbency that make them useful in applications such as medical sponges, means of water retention for agricultural needs, baby diapers, etc.$^{1)}$.

Since they are water soluble, it is often more practical to make acrylic acid polymers in an inverse-phase suspension - i.e. an heterophase water-in-oil polymerisation process. This involves the dispersion of an aqueous monomer(s) solution in a continuous aliphatic phase. Non-ionic steric stabilisers are blended to achieve an overall hydrophilic-lipophilic balance (HLB) of 4-6 to prevent particle coalescence$^{2)}$. In the inverse suspension process, each particle behaves as an isolated batch microreactor. Thus, it seems reasonable that the reaction scheme is much the same as it is for bulk or solution polymerisation. However a large number of parameters influence acrylic acid polymerisation, such as pH, monomer and initiator concentration, temperature, added crosslinker and comonomer. In addition, the ionic strength of the dispersion plays a key role in the number of particles and the reaction kinetics. In the

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present work, we will examine the process for the inverse suspension polymerisation of an aqueous solution of partially neutralised acrylic acid. The influences of surfactant concentration, initiator concentration and stirring speed, as well as the nature of the continuous phase on the system used, were studied.

Experimental

Acrylic acid monomer, sodium hydroxide and potassium persulphate were supplied by ACROS-France and used as received (chemical purity), heptane was used as the organic phase, and Span60 (Sorbitan Monostearate $C_{24}H_{46}O_6$) as the surfactant, and deionized water. In solution experiments, no surfactant or heptane phase was used.

An aqueous solution of acrylic acid was partially neutralised with NaOH. Unless otherwise noted, the degree of neutralisation was 75% which seems to be representative of commercially viable products. A thickener and complexing agent were then added to the aqueous mixture. The continuous phase was prepared by adding heptane and Span60 to a 1000ml round-bottomed flask with a reflux and a stirrer, which was heated in a water bath. The heptane solution was transferred to a 1 litre jacketed glass reactor with a water-cooled jacket. Potassium persulphate in aqueous solution was added to the sodium acrylate solution at room temperature immediately before starting the reaction, and this mixture was added to the reactor under vigorous agitation. The reaction was carried out under nitrogen with vigorous stirring at 70°C.

Several different runs were carried out to study the influence of initiator concentration, stirring speed and surfactant concentration on the reaction kinetics. Details are shown in Table 1. Overall conversion was measured by gravimetry. Samples were

Table 1. Parameters studied.

Sample	Surfactant	[KPS]	Stirring speed
Run 17	1% wt	0.26% wt	600 rpm
Run 20	1%	**0.47%**	600
Run 21	1%	**0.65%**	600
Run 22	**2%**	0.26%	600
Run 23	**3%**	0.26%	600
Run 31	1%	0.26%	**400 rpm**
Run 32	1%	0.26%	**900 rpm**

removed from the reactor and the particles were washed with large amount of methanol (which is possible because particles are self-crosslinked due to chain transfer reaction) and filtered. The resulting poly(sodium acrylate), which was a white powder, was recovered by drying the filtrate in an oven at 90°C.

Results

The influence of varying the different parameters with respect to the base case recipe (Run 17 in Table 1) was studied by looking at overall conversions and by evaluating the overall kinetic rate constant for the reaction. This overall constant is simply the ratio of the propagation constant to the square root of the termination rate constant: $k_p/k_t^{0.5}$. This was found by solving the standard rate expression for free radical polymerisation in batch to yield an expression of the form [3]:

$$\ln(1-x) = -\frac{k_p}{\sqrt{k_t}}\sqrt{\frac{8f[I]_0}{k_d}}\left(1-e^{\frac{-k_d t}{2}}\right) \tag{1}$$

where x is the overall conversion, f the initiator efficiency, $[I]_0$ the concentration of initiator at time zero, and k_d the initiator decomposition constant. If values of k_d are available as a function of temperature, one graph can ln(1-x) vs. $\sqrt{8f[I]_0/k_d}\,(1-\exp(\frac{-k_d t}{2}))$ The slope of this curve gives us a value of $k_p/k_t^{0.5}$ at each instant in time. Thus, if the classical model of free radical solution polymerisation can be applied to this system, it should be possible to find $k_p/k_t^{0.5}(t,T)$ for the different experiments. These values can then be evaluated using an Arrhenius plot to find an overall activation energy for the system. Results are shown in Figures 1-3.

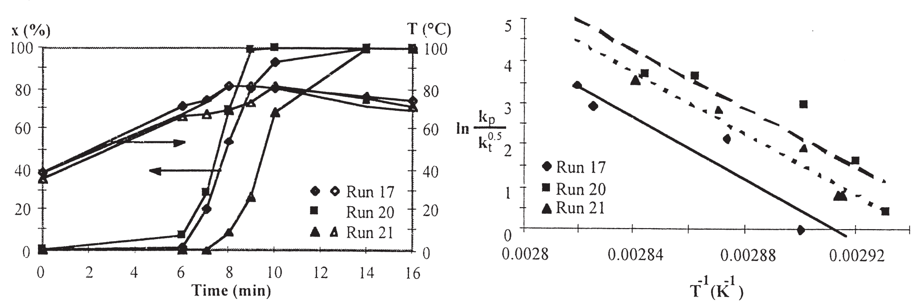

Figure 1. Kinetic study at different initiator concentrations. Conversion and temperature vs. time (left), and Arrhenius plot for corresponding values of the overall rate constant (right). Temperature shown with open symbols, conversion with filled symbols.

One of the more striking features of the polymerisation of partially neutralised acrylic acid is the extremely high reaction rates that are observed for all of the polymerisations. This is accompanied by a significant release of heat and thus an increase in the temperature of the reaction - an autoaccelerating cycle that leads to essentially complete conversion in less than 10 minutes of reaction time (once any initial inhibition period has passed).

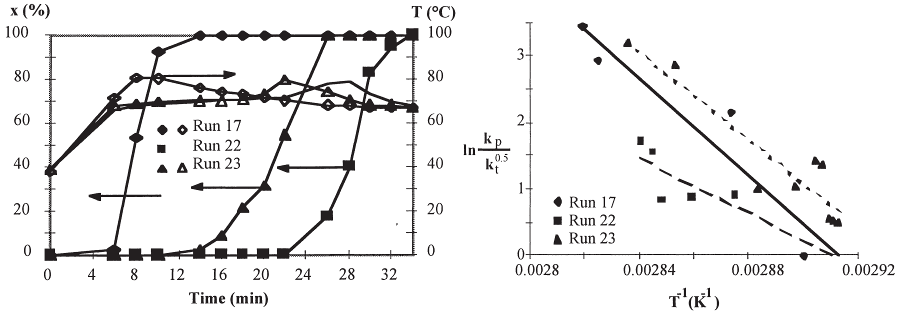

Figure 2. Kinetic study at different surfactant concentrations. Conversion and temperature vs. time (left), and Arrhenius plot for corresponding values of the overall rate constant (right). Temperature shown with open symbols, conversion with filled symbols.

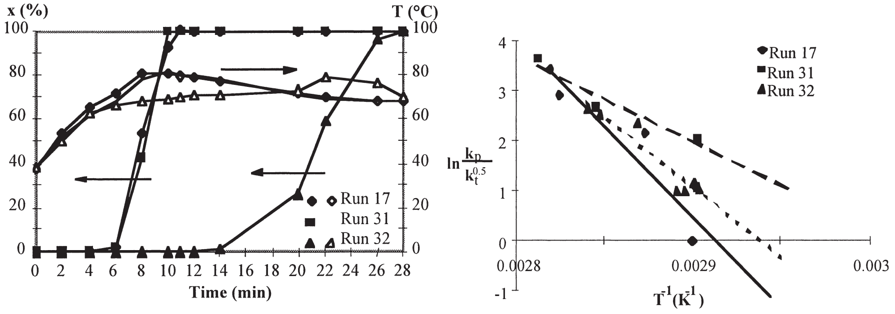

Figure 3. Kinetic study at different stirring rates. Conversion and temperature vs. time (left), and Arrhenius plot for corresponding values of the overall rate constant (right). Temperature shown with open symbols, conversion with filled symbols.

As can be seen in Figure 1, increasing the initiator concentration within the limits shown had little effect on the reaction. This is not particularly surprising, as doubling the initiator should only increase the total radical concentration by at most 41%. However, it turns out that if one cuts down the initiator concentration too much, the increase in particle viscosity due to polymerisation is too slow, and we get massive particle agglomeration in the reactor. Thus, it was not possible to obtain stable dispersions for initiator concentrations of much less than

0.26% (wt monomer). This problem might be overcome by adding very large quantity of surfactant, but this is not really a realistic alternative from a process point of view.
It can be seen from Figure 2 that increasing the stabiliser concentration while holding all other parameters constant seemed to have a slight inhibiting effect on the reaction, although it is uncertain that this is due to the surfactant itself. Other experiments also show inhibition or induction periods of approximately the same length. This might in fact be due to the presence of trace quantities of inhibitors in the stock solutions or in the surfactant itself.

Finally, the polymerisation is probably unaffected by stirring rate at 400 and 600 rpm, as the temperature and the x(t) profiles are very similar for both of these speeds. However, at 900 rpm, particle agglomeration is so important that it became impossible to obtain representative samples. This explains the deviations observed in the rate and Arrhenius plots. Thus, increasing the stirring rate too quickly leads to an inertia induced agglomeration of the particles in the reactor.

Table 2. Values of apparent rate constants

Sample	$k_p/(k_t)^{0.5}$	A_o	E_{app} (kJ/mol)
Run 17	31	5.10^{26}	171,4
Run 20	40	$7,25.10^{19}$	156,3
Run 21	33	$1,1.10^{26}$	171
Run 22	28	$3,56.10^{28}$	196
Run 23	30	$7,64.10^{33}$	215,7
Run 31	39	$2,52.10^{31}$	207,7
Run 32	25	$3,32.10^{32}$	212,8

$$A = \frac{k_p}{k_t^{1/2}} = A_o \exp\left(\frac{-E_p + \frac{1}{2}E_t}{RT}\right) = A_o \exp\left(\frac{-E_{app}}{RT}\right)$$

The values of the apparent activation energies found from Figures 1-3 are summarised in Table 2. It turns out that the E_{app} is very large for most of the experiments : 171.4kJ/mol for Run 17 vs. about half that for similar values in the literature$^{4,5)}$. Kabanov et al.$^{4,5)}$ measured the variations of propagation and termination constants, k_p and k_t for an acrylic acid solution (AA), concentration 1.2 mol.l^{-1}, with pH adjusted with a sodium hydroxide solution and showed that the rate of polymerisation, as well as the apparent values of the rate constants k_p and k_t are very strong functions of pH. This type of phenomenon might explain the high, and highly variable values of E_{app} found in this work, and suggests that using equation (1) to model these systems with constant kinetic parameters is probably not acceptable! More work needs to be done on this point, and will be discussed in a future publication.

Note that we have also not discussed the influence of reaction parameters on particle size in this series of experiments. It turns out that the average particle diameter for most of the experiments where there was no agglomeration was on the order of 10μm, regardless of stirring rate, or initiator and surfactant concentration. This very low value is most likely due to low values of interfacial tension of the system considered here. As shown in Table 3, Span 60 ($C_{24}H_{46}O_6$), in association with acrylic acid causes a dramatic decrease of interfacial tension (2mN/m) in systems where the aqueous phase is dispersed in either heptane or toluene. When acrylic acid is neutralised at only 75% (which is the neutralisation rate used during the kinetic study), -COOH groups may be at the heptane/particle interface. It was therefore not useful to study the relationship between particle size and conditions. It appears that the only way to vary particle size would be to alter the viscosity of the dispersed and/or dispersing phase, or to change the dispersing phase in order to alter the interfacial tension.

Table 3. Interfacial tensions for dispersions of aqueous solutions of partially neutralised AA

Aqueous phase	Organic phase	Interfacial Tension (mN/m)
AA neutralised **75%**	heptane + span 60(1%)	1.8
AA neutralised **50%**	heptane + span 60(1%)	1.6
AA neutralised **100%**	heptane + span 60(1%)	1.1
AA neutralised **75%**	toluene + span 60(1%)	1.5
AA neutralised **55%**	toluene + span 60(1%)	1.9
AA neutralised **100%**	toluene + span 60(1%)	1.1

Conclusions

The two most important aspects influencing the stability and kinetics of the inverse suspension polymerisation of partially neutralised acrylic acid seem to be the initiator concentration and stirring rate. If the initiator concentration is not high enough, the particles remain sticky too long in the reactor and coalesce. On the other hand, if the stirring rate is too high, this causes the particles to agglomerate.

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