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Contributions to defining the rate constants for the homo- and copolymerisation of butyl acrylate and vinyl acetate

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Summary

Free radical homo- and copolymerisations of vinyl acetate and butyl acrylate were carried out in solution. Initial differences in data from homopolymerisation experiments lead us to investigate the influence of an eventual oxygen inhibition on the observed rate of polymerisation.

A kinetic study at 70 °C was carried out both with and without a nitrogen purge. A decrease in the rate of polymerisation in the second instance was attributed to the presence of dissolved oxygen in the solution. Estimates of the apparent inhibition constant from different experiments are used to model both homopolymerisation and copolymerisation with vinyl acetate. The importance of taking this phenomenon into account during kinetic studies is demonstrated.

Experimental

The solution homopolymerisation of vinyl acetate (VAc), and the copolymerisation of vinyl acetate and butyl acrylate (BuA) were carried out in an ethyl acetate (EAc) solvent using benzoyl peroxide (BPO) as the sole free radical initiator.

The monomers and solvent were obtained from Janssen Chimica (France) and used without further purification. The feed policies for each of the five different types of experiments are given in Table 1

Runs 1-3 and 6 were batch reactions, Run 4 a semi-batch reaction with addition of butyl acrylate, and Run 5 a semi-batch reaction with addition of a mixture of both monomers and solvent (with a tail of butyl acrylate). Samples were occasionally withdrawn from the reactor, the times and quantities of which were noted for use in calculating conversions and closing the mass balance equations.

Reactions 1,2 and 6 took place in a 2-litre stirred reactor equipped with a cooling jacket, and inlet and outlet valves for nitrogen purge. The other reactions took place in a 7-litre stirred tank equipped with a cooling jacket and condenser. Water was circulated through the jacket to maintain the reactor and its contents at 70 °C. The flow rates of the components added during semi-batch operation (Runs 4 and 5) were recorded by placing the monomer reservoirs on a digital scale, which was in turn connected to a microcomputer.

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Table 1. Feed policies for polymerisation experiments. All reactions at 70°C.

Run Number	Reactor Heel	Addition Policy
1	200g BuA, 800g EAc 1.34 g BPO	Batch Reaction - No additional feeds Distilled Monomers
2	200g VAc, 800g EAc 1.34 g BPO	Batch Reaction - No additional feeds Distilled Monomers
3	749 g BuA, 3000 g EAc 5.0 g BPO	Batch Reaction - No additional feeds
4	373 g VAc, 77 g BuA 3000 g EAc, 5.15 g BPO	300 g BuA added continuously over 3 hour period.
5	150.8 g VAc, 43.3 g BuA 1419.5 g EAc 5.2 g BPO	Mixture of 228.5g VAc + 173.5g BuA + 1584g EAc added for 3.1 hours. Then 40g BuA added over 24 minutes. Polymerisation lasted 5.6 hours
6	200g BuA, 800g EAc 1.34 g BPO	Batch Reaction - No additional feeds. No nitrogen purge used at all.

The nitrogen purge in Runs 1 and 2 was accomplished using sealed joints designed for this task. In Runs 3-5, the nitrogen was introduced through the condenser of the 7-litre reactor, and in each of these cases no attempt was made to seal the opening (on the order of 1.5 cm in diameter) during the experiment. Also, during Runs 4 and 5, the monomer was added through an opening in the lid of the reactor and the space between the feeding tube and the edge of the opening was sealed with paper towelling. The same was true for the opening of the monomer reservoir. In Run 6, the outlet valve of the reactor was left open. It should also be noted that the distance between the nitrogen inlet and the reaction mixture in Runs 3-6 was on the order of 0.75 m, whereas it was on the order of only a few centimetres for Run 6.

Results and Discussion

A comparison of the butyl acrylate homopolymerisations are shown in Figure 1. It is quite obvious that, although one would initially expect them to be similar, the rate of polymerisation in Run 3 is significantly lower.

The data from Run 1 (solid line) can be modelled using the classic free radical polymerisation equations with the data given in Table 2, and using a value of $k_p / k_t^{1/2} = 0.94$ at 70°C to fit the data. It was assumed that the termination rate was not influenced by the gel effect, a reasonable simplification in a system where the maximum polymer concentration is on the order of 20%.

The same value of $k_p/k_t^{1/2}$ does not appear to describe the kinetics of Run 3. However, it should be recalled that Runs 1 and 3 differed in that the reactor in Runs 3-6 was less well sealed against the external environment. This means that it is quite reasonable to suppose that oxygen remained dissolved at a more or less constant concentration throughout the experiments carried out in Runs 3-6. It is well-known that oxygen can have an inhibiting effect on the reaction, and this can be used to explain the lower observed rate of Run 3 in Figure 1.

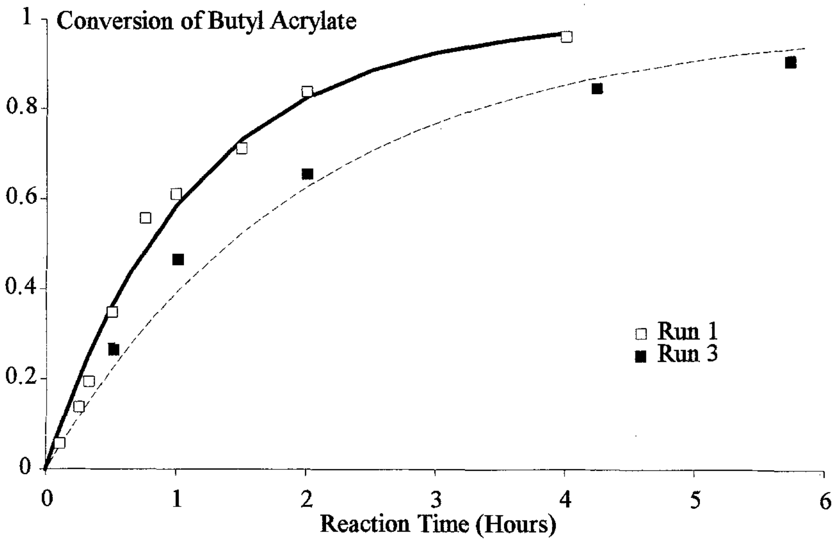

Figure 1. Experimental conversions of BuA (70°C). Solid curve is classic FRP model with $k_p / k_t^{1/2} = 0.94$. Dashed curve is same model with $k_z[Z] = 0.08$.

Table 2. Physical Properties of Reaction Components (All kinetic constants reported at 70°C)

Property	Vinyl Acetate	Butyl Acrylate
Density (g/cm^3)	0.932 (60°C)[1]	0.89 (60°C)[1]
Homopol. density(g/cm^3)	1.15 (70°C)[2]	1.08 (25°C)[3]
k_p (l/mol/s)	5940 [4,5,6]	264 [4,5,6,7]
E_{Ap} (kCal/mol-propagation)	6.3[8]	6.3[8]
$k_p / k_t^{1/2}$ (at 70 °C)	0.279[a]	0.978[a]
E_{At} (kCal/mol-termination)	2.8[8]	2.8[8]
k_{fm} (trans. to monomer: l/mol/s)	1 (to self) [9,10,11] 0.01 (to BuA)[est. from 11]	0.05 (to self) [11] 0.01 (to VAc) [est. from 11]
k_{fp} (trans. to polymer: l/mol/s)	3 (to self) [9,10,11] 3 (to PBuA)[b]	0.4 (to self) [11] 0.4 (to PVAc)[b]
k_{fp} (trans. to solvent: l/mol/s)	3 [est. from 11]	0.025 [est. from 11]
ΔH_p (kCal/mol)	21[12]	18[12]
r_1	4.5[est. from 13,14]	0.012 [est. from 13,14]
k_d (BPO)	$.69 * 104 \exp\left(-30000/RT\right)$[2]	
Density of EAc (g/cm^3)	0.895 (25°C)[a]	

[a] Experimental [b] Best Guess

In the event that an inhibitor is present, the free radicals formed from the decomposition of a chemical initiator at a rate $R_I = 2fk_d[I]$ are destroyed by reacting with an inhibitor to produce an non-reacting molecule, and through the normal termination reactions. The equation describing the rate of generation/consumption of free radicals is:

1) $$\frac{\partial[R^*]}{\partial t} \approx 0 = 2fk_d[I] - k_t[R^*]^2 - k_z[Z][R^*]$$

where [R*] is the concentration of free radicals, f the initiator efficiency, k_d the initiator decomposition rate, [I] the concentration of initiator, k_t the lumped bimolecular radical termination constant, k_z the inhibition constant, and [Z] the concentration of inhibitor, in this case oxygen. Invoking the quasi-steady state hypothesis, and assuming that the inhibitor concentration remains constant leads to the following expression for the radical concentration:

2) $$R^*] = \frac{-k_z[Z] + \sqrt{(k_z[Z])^2 + 4(2fk_d[I]k_t)}}{2k_t}$$

It can be seen that when [Z]=0 (2) collapses to the well-known $R^*] = \sqrt{\frac{2fk_d[I]}{k_t}}$.

From equation (2) it can be seen that under conditions where there is a constant inhibitor concentration, as is presumed to be the case in Runs 3-6, then it is not necessary to know both the inhibition rate constant and inhibitor concentration independently, the rate of conversion of monomer can be modelled if we know the product $k_z[Z]$. A value of $k_z[Z] = 0.08$ (at 70°C) seems to fit the Run 3 data well (dashed curve in Figure 1.)

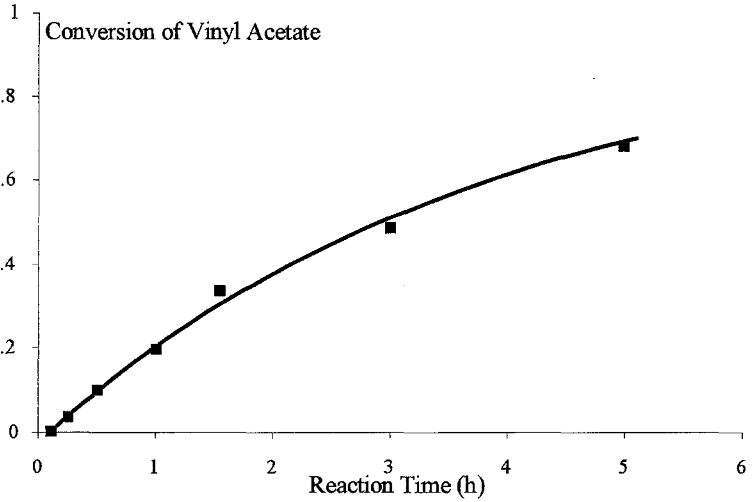

Figure 2. Run 3 plus model prediction for the homopolymerisation of vinyl acetate at 70°C (Run2).

An experiment similar to Run 1 was carried out for distilled VAc (Run 2 - well-sealed reactor), the results of which are shown in Figure 2. A brief period of inhibition due to some remaining stabiliser is apparent at the beginning of this reaction, but once this is removed, a value of $k_p/k_t^{1/2} = 0.28$ (at 70°C) fits the data very well. It was assumed that there was no secondary inhibition due to dissolved oxygen in Run 2 once the reaction began.

Absolute values of the propagation constants k_p for each of the monomers were estimated from the literature (see Table 2) and used along with the experimental values of $k_p/k_t^{1/2}$ to simulate the copolymerisation experiments of Run 4. Given the observed reaction conditions, it was assumed that dissolved oxygen was present at levels similar to those in Run 3 during this experiment. The simulation results with $k_z[Z] = 0.08$ are shown in Figure 3. The agreement between model and experiment is satisfactory.

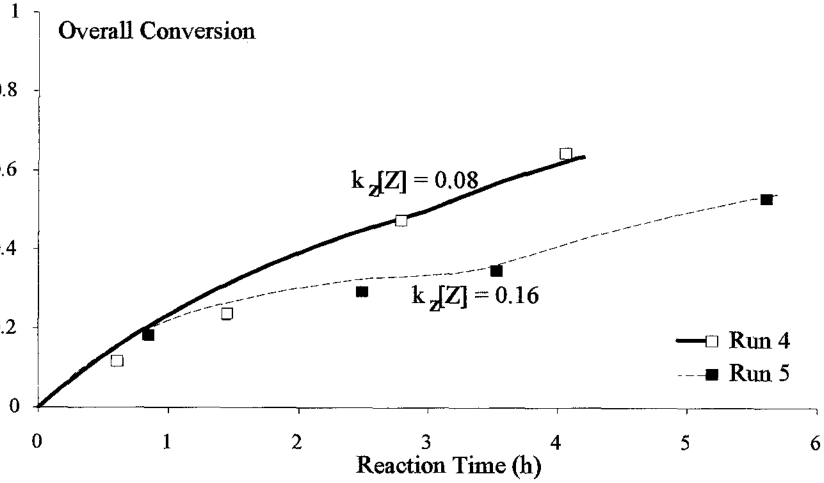

Figure 3. Simulation of Runs 4 and 5 using homopolymer data, estimated inhibition constant and literature data.

However, using a similar value of $k_z[Z]$ does not lead to an adequate agreement between the model predictions and Run 5, and one must increase the value of this pseudo-constant to 0.16 in order to obtain a good fit of the data. It is important to know whether or not this treatment is justifiable, or if the differences between the two Runs are due to deficiencies in the classic kinetic model of copolymerisation.

It would seem that increasing the value of $k_z[Z]$ is a valid action for two reasons. First of all, the direct extension of the homopolymerisation results to the copolymerisation in Run 4 seems to indicate that this modelling approach provides reliable predictions. Second, although reaction conditions were similar for Runs 4 and 5, and the monomers and initiator taken from the same batches of product, the reactions were performed on subsequent days and it is thus reasonable to suppose that somehow slightly more oxygen was present in the gas phase of the reactor, and therefore more of it was dissolved in solution, during this second copolymerisation experiment.

Run 6, which is essentially identical to Run 1 without any nitrogen purge, was performed in order to investigate the sensitivity of this reaction system to oxygen concentration. In this case, the condenser on the reactor was left open to the ambient atmosphere and no nitrogen purge was used during the reaction. It can be seen from

Figure 4 that in this Run the reaction rate dropped to extremely low values, and a value of $k_z[Z] = 2$ is needed to give a reasonable fit to the data. Admittedly, there is more scatter here than in the other runs, and the value of $k_z[Z] = 2$ is only approximate.

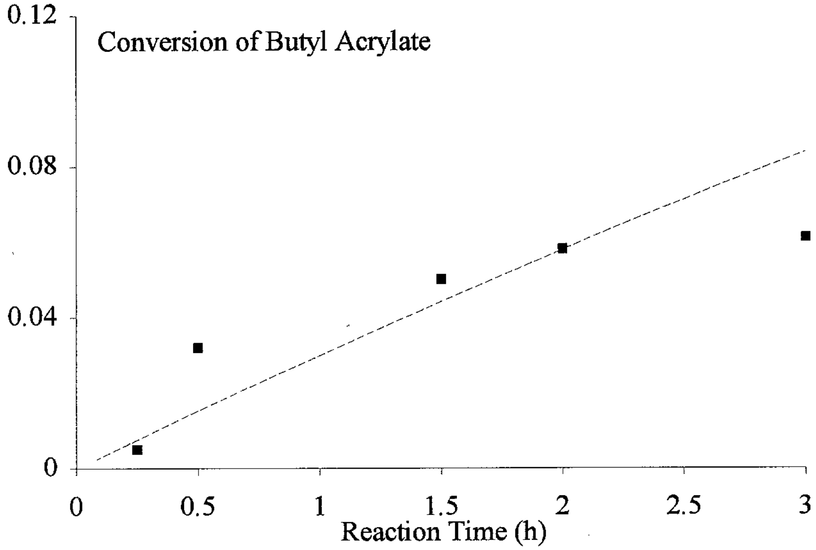

Figure 4. Run 6 results (points) and model predictions with $k_z[Z] = 2.0$.

We can therefore conclude that the rate of reaction is very sensitive to dissolved oxygen, and that potential differences in the importance of the leaks in the reactor system between Runs 4 to 5 could lead to a situation where the amount of oxygen present in the gas phase of the reactor essentially doubled from Run 4 to Run 5 experiment.

It should be noted in making this last comment that it can be said that the amount of oxygen possibly present in the gas phase during Runs 4 and 5 is much lower than the ambient value of 0.21 atm. While the reactor was not well-sealed during Runs 4 and 5, it was partially closed and there was a constant stream of nitrogen sweeping out the gas phase. Thus, the any oxygen present would be in rather small quantities. We can use the results of Run 6 to estimate approximately how much oxygen was present. According to Linke [15] the Ostwald solubility (volume of gas/volume of liquid) of oxygen in ethyl acetate is on the order of 0.175 at STP (1 atm., 25°C). Assuming ideal gas behaviour it is possible to show that this corresponds to an equilibrium solubility of oxygen on the order of 0.004 mol/l for 1 atm. of oxygen. The solubility of oxygen in air will be 1/5 of this value, i.e. on the order of $8*10^{-4}$ mol/l at 25°C. Using idealised thermodynamic relationships (Clapeyron equation), we can estimate the equilibrium solubility of oxygen in EAc at 70°C to be on the order of $8*10^{-5}$ mol/l. Supposing that the solubility of oxygen is similar in all of the components of the mixture, and that the concentration of oxygen in the gas phase of Run 6 is approximately that of air (i.e. the concentration of oxygen in the liquid phase is at equilibrium at all times), then we can estimate that k_z = 25,000 sec^{-1}. Using this result and assuming that k_z remains constant from one Run to the next, we may conclude that the oxygen concentration in Run 4 was on the order of $3.2*10^{-6}$ mol/l, and 6.4 $2*10^{-6}$ mol/l in Run 5. These concentrations correspond to partial pressures of oxygen in the gas phase of the reactor of 0.008 and 0.017 atm. respectively. Even if the value of the inhibition constant of oxygen is in error, it is nevertheless clear that the kinetics of this system are sensitive to even very small concentrations of oxygen, and the variation the product $k_z[Z]$ from Run 4 to Run 5 can be explained in this manner.

On a slightly different note, in modelling the termination rate of the copolymerisation experiments, the cross-termination constant, usually assumed equal for the two monomers is described by the equation:

$$3) \qquad \phi = k_{t_{12}} \Big/ \sqrt{k_{t_{11}} k_{t_{22}}}$$

where ϕ is an experimentally determined empirical factor. In the modelling studies presented above it turned out that, if we accept the parameter values in Table 2, $\phi = 1$

Conclusions

In this paper we have presented values for the pseudo-rate constants $k_p/k_t^{1/2}$ for the homopolymerisation of Butyl Acrylate and Vinyl Acetate. The agreement between the simulated values and experimental results is satisfactory, and is thus safe to say that the values of $k_p/k_t^{1/2} = 0.978$ for BuA and $k_p/k_t^{1/2} = 0.279$ for VAc are correct for their solution polymerisation (both homo- and copolymerisations) in EAc at 70°C when the gel effect can be safely neglected. Literature values for this ratio varied over a wide range - from below 1 to over 100 for BuA, and from 0.3 to approximately 10 for VAc at the range of temperatures in question [1-5,7,9-11] - and therefore this data is of use in helping to define kinetic constants for this system. The data presented here tend to agree with the lower end of the interval of values reported in the literature.

Furthermore, the success of applying batch homopolymerisation data to two semi-batch copolymerisation reactions carried out in different reactor systems confirms the validity of the rate constant data reported here (i.e. the absolute values of k_p and k_t selected from the literature for the two monomers), and reinforces the interest of eliminating potential contributions from inhibitors in the system when performing kinetic experiments, especially those such as oxygen which may be continually present, especially in continuous industrial reactors. A very approximate value of the inhibition constant of oxygen is also reported and found to be on the order of 25,000 sec^{-1}.

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