Polymer Bulletin 47, 269–275 (2001)

Polymer Bulletin

Decomposition of APS and H_2O_2 for emulsion polymerisation

M. Schneider, C. Graillat, S. Boutti, T.F. McKenna (✉)

LCPP-CNRS/ESCPE-Lyon, Bât 308F, 43 Blvd du 11 Novembre 1918,
69616 Villeurbanne CEDEX, France,
e-mail: mckenna@cpe.fr, Tel.: (33) 4 72 43 17 75, Fax: (33) 4 72 43 17 68

Received: 24 July 2001 /Accepted: 12 October 2001

Introduction

The role of the free radical initiator in emulsion polymerisation is essentially to provide a reliable source of free radicals for the nucleation of particles, to initiate the propagation reaction, and, in certain cases, to help stabilise particles (e.g. when polymerising in the absence of any surfactant). It is clear that if we are to either model a polymerisation reaction, or to develop recipes in the laboratory, it is necessary to know the decomposition behaviour of the initiators we are going to use. In most industrial contexts one relies on initiators that decompose either when they are heated, either alone or in the presence of an activator.

We will look at two different initiators in this work: (1) ammonium persulphate (APS), which is a hydrosoluble initator, and (2) the redox pair of hydrogen peroxide and ascorbic acid (HPO/AscA). APS is commonly used in an number of industrial recipes, and although one would suspect that its decomposition kinetics would be similar to those of potassium persulphate (KPS) or sodium persulphate (NaPS), very little information is available on the value of k_d, its decomposition constant, in the literature. APS decomposes to yield negatively charged sulphate radicals without the aid of an activator, but its decomposition can be accelerated by adding a compound such as a bisulphite. It is well known that it is possible to make emulsions without surfactant with this type of initiator because the negatively charged free radicals help to stabilise the polymer particles. This can pose a problem when trying to maintain strict control over the particle size distribution (PSD) when polymerising water-soluble monomers (e.g. MMA) [e.g. 1].

It has been shown [1] that replacing APS with an uncharged generator of free radicals (e.g. HPO) alters the stability of a polymerising system and can be used to surpress stabilisation of homogeneously nucleated particles. It is therefore useful to know the decomposition kinetics of the HPO/AscA system in order to optimise polymerisation recipes and to model the reaction. HPO decomposes in the presence of AscA to yield two electrically neutral hydroxy radicals. If HPO is not used in a redox system, there must be a continual supply of AscA in order to catalyse its decomposition.

Experimental

We will explore the decomposition of APS in deionised water at temperatures

between 70 and 80°C, and that of HPO/AscA at 80°C. The reactions are carried out in a 3 litre glass reactor with a heating/cooling jacket attached to a thermostatted batch, and an anchor agitator that is turned at 150 rpm. The reactor was filled with 2 litres of deionised water before each experiment, and sparged with nitrogen for half an hour. A PT100 thermocouple is placed in the reactor to monitor the temperature, and a pH meter is used to control the pH. APS, HPO and AscA were all obtained from Aldrich (France) and used as received.

APS

1.8 g/l of APS is injected with a small quantity (2-10 ml) of water into a preheated reactor containing deionised water. Samples were occasionally withdrawn for potentiometric analysis (Titraplus potentiometer from Tacussel, with a XS300 lead specific electrode, also from Tacussel) [2]. The concentration of Pb^{2+} was measured using a lead-specific electrode and a calomel reference electrode. The sulphate ions (SO_4^{2-}) precipitate with Pb^{2+}, so by careful titration we can count the sulphate ions generated by the decompostion of APS. Precipitation of $PbSO_4$ is enhanced by performing the measurements in methanol since the product of the precipitation is partially soluble in water. The actual measurements were done automatically. 1 gram of the decomposing APS solution is mixed with 60 ml of methanol. Titration is begun once the potential of the mixture stabilises to a fixed value. The potentiometer reservoir contains 10 ml of the titrating solution, which is a 3.3 mmol/l solution of lead(II)perchlorate (LPC). This was prepared by mixing 0.37 g of LPC with 250g of demineralised water at room temperature. Since this solution is not very stable, it was prepared just before each titration. The concentration of the LPC solution was verified by titration with a sulphuric acid solution after each preparation.

HPO/AscA

Reactions are carried out in deionised water at 80°C with an initial composition of 3 g/l of HPO, with and without AscA. Two different runs were performed: in one run no AscA was used, in the second, 3 g of AscA were injected after 7h. The decomposition of HPO is measured using manganimetry. The principle of the method is based on the titration of a solution of potassium permanganate as shown below:

$$2(K^+,MnO_4^-) + 5\ H_2O_2 + 3\ H_2SO_4 \rightarrow (2K^+,SO_4^{2-}) + 2\ (Mn^{2+},SO_4^{2-}) + 2\ H_2O + 5\ O_2$$

5 g of HPO solution is mixed with 15 ml of demineralised water and 10 ml of a 2 M solution of H_2SO_4. Titration is done by hand with a graduated pipette, and is complete when the solution, which is originally colourless, turns violet due to an excess of permanganate.

Semibatch copolymerisations of butyl acrylate (BA) and methylmethacrylate (MMA) were performed to demonstrate the feasibility of manipulating the reaction rate with AscA. The reaction was run by charging the reactor with 300 g of deionised water, 20 g of MMA and 80g of BA. A mixture of 0.02 g of Disponil® FES 32 IS (sodium salt of the sulphate of a polyglycol ether), and 2.7 g of Disponil® A 3065 (mixture of linear ethoxylated fatty acids) was dissolved in one litre of deionised water along with 1 g of H_2O_2. Both surfactants were supplied by Cognis (France) and used as received.

This mixture was stirred until homogeneous, and then added to the reactor. The reactor contents were degassed for 15 minutes with nitrogen, stirred at high speed (350 rpm) for 5 minutes to ensure that the contents were correctly dispersed while being heated to 70°C. The reaction was begun by injecting 1 g of a solution 2.52% (w/w) solution of AscA (equivalent to 1.4×10^{-4} mol/shot). Additional pulses of AscA were injected at 90, 180, 270 and 360 minutes. Samples were occasionally withdrawn to follow the conversion by gravimetry, and to measure the average particle size by quasielastice light scattering (Malvern Autosizer Lo-C).

Results

Figure 1 shows the results for APS at 70° and 80°C. The rate constants for the decomposition of APS (k_d) and the half lives ($t_{1/2}$) are calculated from the slope of the line, which represents the natural logarithm of the fraction of APS left in solution divided by the original concentration as a function of time. At 70 and 80° C, the following results were obtained:

$k_d = 4.3\cdot10^{-5}\ s^{-1}$ $\quad t_{1/2} = 4.4$ hours (264 min)
$k_d = 1.6\cdot10^{-4}\ s^{-1}$ $\quad t_{1/2} = 1.2$ hours (72 min)

Santos et al. [1] measured these same quantities for a 2.7 mmol/ solution of KPS (vs 3.3 mmol/l of APS used here). They found values of $k_d = 4.31\cdot10^{-5}\ s^{-1}$ and a half life of 273 minutes for that initiator under conditions where the pH was free to vary during the experiment. The results are clearly similar to what we find for APS, suggesting that the persulphate family of initiators all have very similar values of k_d under typical industrial conditions.

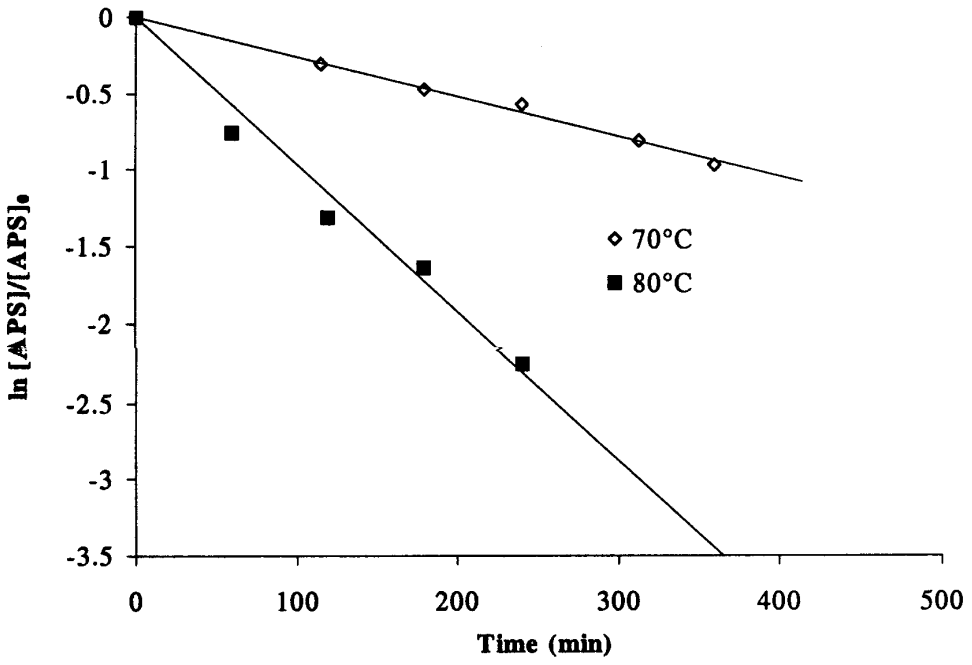


Figure 1. Decomposition of APS at 70° and 80°C as a function of time.

Although we must do so with caution as we have used only 2 temperatures, we can deduce that the activation energy of APS is 131.6 kJ/mol for the temperatures studied here. This result is coherent with those available for other persulphate initiators that can be found in the Polymer Handbook [3]; e.g. the activation energy for the decomposition of KPS is reported as being in the range of 83.4-140.2 kJ/mol (and in general for free radical initiators used in the temperature range in question).

We can see from Figure 2 that the decomposition behaviour of HPO is quite different. Effectively, when HPO is decomposed on its own, the reaction is extremely slow, even at 80° C. In fact the half life of HPO alone at 80° C is 144 hours (8640 minutes, or 6 days), and the k_d is approximately $1.33 \cdot 10\text{-}6\ s^{-1}$ at the same temperature - 2 orders of magnitude lower than that of APS. However, when the decomposition takes place in the presence of ascorbic acid, the rate of reaction is considerably accelerated. However, the effect of AscA is (relatively) short lived, as we can also see from Figure 2. Here it can be seen that the slope of the fraction of HPO remaining is much higher when the medium contains AscA. For instance, the solution of HPO in the second experiment initially contained 3 g/l of AscA in addition to the HPO. However, this is consumed in approximately 100 minutes. Once the AscA disappears, the slope of the decomposition line quickly reverts to the same value as without the acid. A second injection of 3 g of AscA quickly reaccelerates the decomposition to the same rate as previously noted at the beginning of the experiment. In effect, injecting 1 mole/l of AscA at the beginning of the reaction allows us to consume approximately 20% of the HPO (initial concentration 5.2 moles/l).

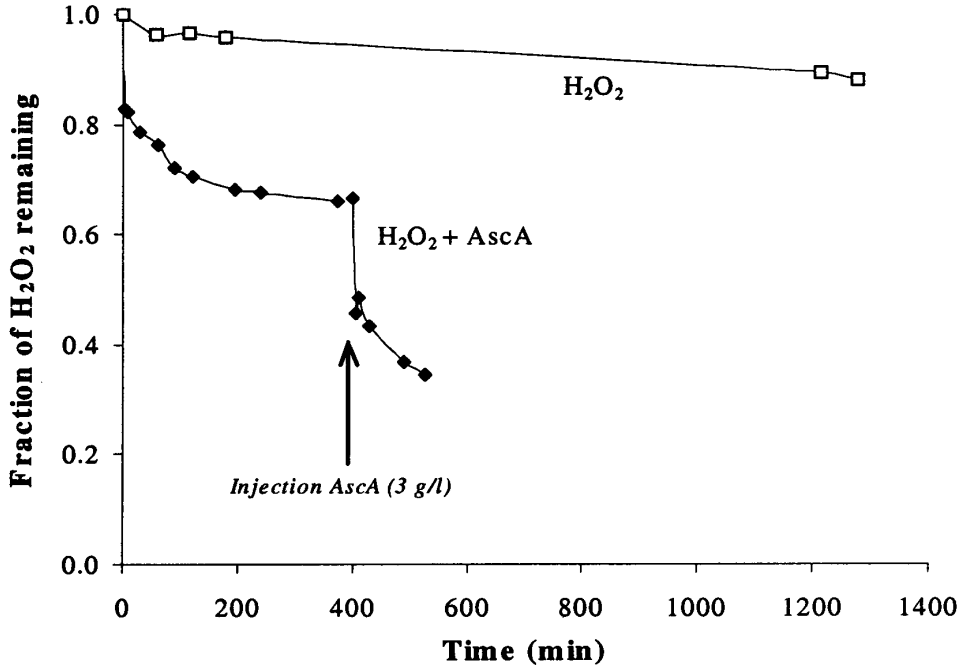


Figure 2. Decomposition of H_2O_2 with and without AscA at 80°C. The decomposition is excessively slow without the AscA, which in turns seems to be consumed very quickly.

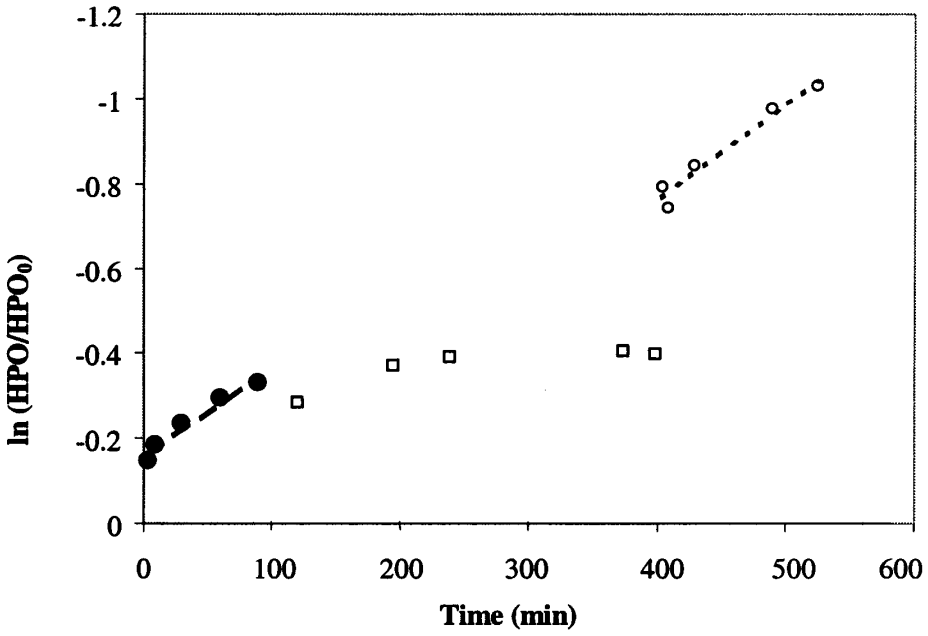
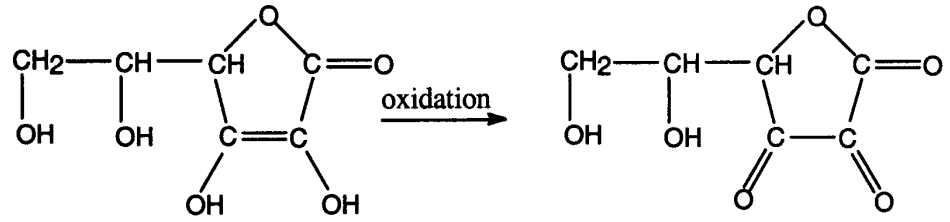


Figure 3. Natural logarithm of the fraction of HPO remaining as a function of time. Axis has been changed to allow calculation of k_d in s^{-1}. For times less than 5400 s (90 min), $k_d = 3.4 \cdot 10^{-5}$ s^{-1} and above 25000 sec (417 min), $k_d = 3.8 \cdot 10^{-5}$ s^{-1}.

Figure 3 shows the calculation of k_d. The value of the rate constant is calculated from:

$$\ln\left(\frac{HPO}{HPO_0}\right) = -k_d t$$

In the regions where we still have AscA, the average value rate constant is found to be on the order of $3.6 \cdot 10^{-5}$ s^{-1} ($3.4 \cdot 10^{-5}$ s^{-1} during the initial decomposition stage, and $3.8 \cdot 10^{-5}$ s^{-1} after the second addition of AscA). This result suggests that as long as there is AscA in solution, the characteristic rate coefficient of the decomposition reaction is constant, and the reaction is first order with respect to the concentration of HPO. However, once the AscA is consumed, the reaction slows down by over one order of magnitude. This activation reaction is probably an oxidation-reduction type of reaction, with the HPO being reduced by the AscA as in scheme I [4,5].



Scheme I

On the one hand, this need for a constant concentration of AscA during the decomposition of HPO can be inconvenient as it adds an additional feed stream and level of complication to the reactor control scheme. On the other hand, as shown by

Schneider [1], this combination of a two part redox initiator system can be very useful when trying to evenly disperse the initiator in a viscous medium. In addition, one can also control the flux radicals in the reactor at any given time with more precision using this type of scheme. This is demonstrated by the copolymerisation experiment shown in Figure 4. Here we see that the rate of polymerisation can be activated at different times by adding shots of AscA (all of the HPO is added at the beginning). This gives us a supplementary control over the rate of reaction during an emulsion polymerisation, and can even allow us to envisage mixed initiator systems that can be activated at different times during the reaction when appropriate (e.g. [6]). Note that there is a slight delay between the injection of AscA and the peak rates observed in this figure. However, it is clear that the slope of the rate curve begins to change immediately after injection of the AscA. This increase in the reaction rate continues for approximately 60 minutes, and then begins to decrease. Given the results in Figure 2, the increase in the rate is due to an increase in the flux of free radicals available for polymerisation. The rate increases each time for approximately 30-60 minutes, then begins to decrease as the concentration of AscA decreases. It is possible that injection of initiator is accompanied by an temporary increase in the number of particles. These particles could be nucleated by a homogeneous mechanism, but since they are not stabilised (see e.g. [6]) they will flocculate onto the larger particles, thereby causing d_p to increase sharply. As the acid is consumed, the rate reaches a peak and then decreases to a local minimum (the value of which depends on the relative concentration of acid and monomer) until the next injection of AscA.

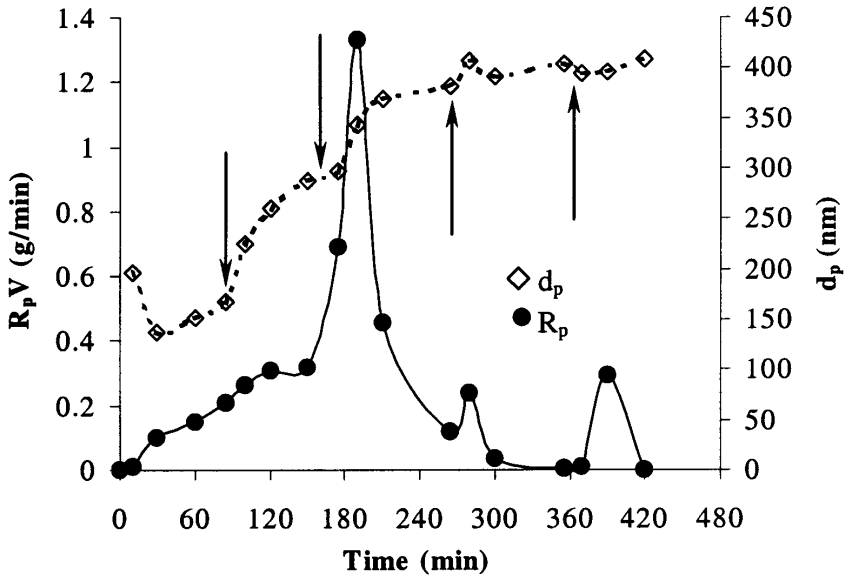


Figure 4. Rate of polymerisation and evolution of particle size for batch copolymerisation of MMA and BA using HPO+AscA. Arrows indicate injections of AscA solution.

Note that we have chosen to look at the decomposition of H_2O_2 under a limited range of concentrations of AscA and initiator. The major motiviation for this limitation was that this concentration range gives us a flux of radicals of the same order of magnitude as we obtain from APS under the conditions needed to produce high solid content

acrylic latexes under industrial conditions [1,6]. It is expected that the pseudo-first order rate constant will be independent of the relative quantites of intiator and acid, as the apparent rate of reaction decreases rapidly to zero once the acid is consumed. Changing the relative quantities would simply change the length of the period during which a constant flux of radicals is produced (see e.g. Figure 4.)

Acknowledgements

The authors are grateful for the financial support of ATOFINA.

References

1. Schneider, M. (2000) Ph.D. Thesis, Université Claude Bernard Lyon I
2. Santos, A.M., Ph. Vindevoghel, C. Graillat, A. Guyot, J. Guillot (1996) J. Polym. Sci., Part A.: Polym. Chem., 34: 1271
3. Dixon, K.W. (1999) Decomposition Rates of Organic Free Radical Initiators, in Brandrup, J., E.H. Immergut, E.A. Grulke (eds.) Polymer Handbook (4th Edition, II1-76),, J. Wiley & Sons, New York
4. Kvernberg, O., B. Pedersen (1994) Acta Chem. Scandinavia, 48: 646
5. Deutsch, J.C. (1998) Analytical Biochemistry, 255: 1
6. Schneider, M., C. Graillat, A. Guyot, T.F. McKenna (Accepted for publication 2001) J. Appl. Polym. Sci.