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Polychloroprene 'popcorn' growth kinetics measured by the McBain balance

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The rate at which chloroprene proliferates or polymerizes by the 'popcorn' mechanism from the vapour has been measured by means of a McBain balance between the temperatures of 3°C and 45°C. First-order kinetics were found for growth over 2 or 3 days once an induction period was complete. The Arrhenius activation energy for the growth was found to be $38.4 \pm 0.7\,\mathrm{kJ\,mol^{-1}}$.

(Keywords: chloroprene popcorn polymerization; kinetics; McBain balance)

Introduction

The spontaneous polymerization of chloroprene, aspects of which we have previously investigated[1,2], was first noticed by Carothers *et al.* when they introduced the monomer[3]. As is probably the case with other diene monomers, such as butadiene[4], which share the 'popcorn' growth or proliferation process, it proceeds by a radical mechanism, for electron paramagnetic resonance (e.p.r.) spectroscopy has found signals in chloroprene popcorn that increase in intensity as the reaction proceeds[1]. Furthermore, initiation of the popcorn takes place readily, on even stainless steel, close to a corrosion site that is likely to be a source of free radicals[2]. Other popcorns have also been shown to contain free radicals by e.p.r. spectroscopy[5]. The radical e.p.r. signal from chloroprene popcorn diminishes quickly upon the addition of species that react readily with the free radicals[1]. The susceptibility of popcorn radicals to such gases as oxygen and the oxides of nitrogen, NO and NO_2, provides a possible route to the control of popcorn growth in both the liquid and the vapour phases, in the plant where chloroprene monomer is handled and where the polychloroprene rubber is produced.

The standard methods of following the kinetics of polymerizations include dilatometry, which is continuously applicable to a reaction in solution, as well as methods such as nuclear magnetic resonance (n.m.r.) spectroscopy that may monitor the disappearance of the monomer and the increase in the yield of the polymer. Chloroprene popcorn growth from the gas phase may have been detected on two occasions; when the monomer pressure was monitored the number of radicals present in the solid phase rose with time[6]. The disappearance of functional groups in a step growth polymerization may be followed by titration[7]. Weight measurements of yield may be made in a single run of an addition polymerization and repeated under different conditions to reveal the kinetic relationship. Weight measurements that we made previously during popcorn growth within the liquid phase had the disadvantage that the liquid had to be removed by vacuum before each weighing of the popcorn could be made, and this undoubtedly led to the growth rate being reduced, for an induction period of a few hours was suggested by the measurements themselves[1]. Furthermore when popcorn grows in contact with the liquid monomer, there may be simultaneous growth of linear polymer and of a lightly crosslinked form, making dilatometry unsuitable[8].

The novel method we now describe allows us to monitor popcorn proliferation by directly and continuously measuring its weight without interrupting its growth. The method may also lend itself to monitoring the effect of gaseous free radical scavengers, such as NO, which are known to react with popcorn radicals[1]. We place pieces of chloroprene popcorn in the bucket of a McBain balance, and monitor the increase in weight of the popcorn as it grows from the vapour by measuring with a travelling microscope the increase in the length of the glass spring that supports the bucket. The diagram in *Figure 1* shows the arrangement of the spring, the bucket, the popcorn and the microscope. As the relationship between the length of the spring and the weight in the bucket is known, the weight of the popcorn may be obtained as frequently as a measurement is made of the length of the spring. In this communication we describe measurements made to determine the rate of growth of chloroprene popcorn over a range of temperatures close to ambient conditions.

Experimental

The apparatus we have used is shown in *Figure 1*. The temperature within the system was monitored with thermometers that recorded the values on paper at intervals of about an hour. Temperatures were constant within the system and over the periods of the growth to within 0.1°C, when varied from about 5°C to about

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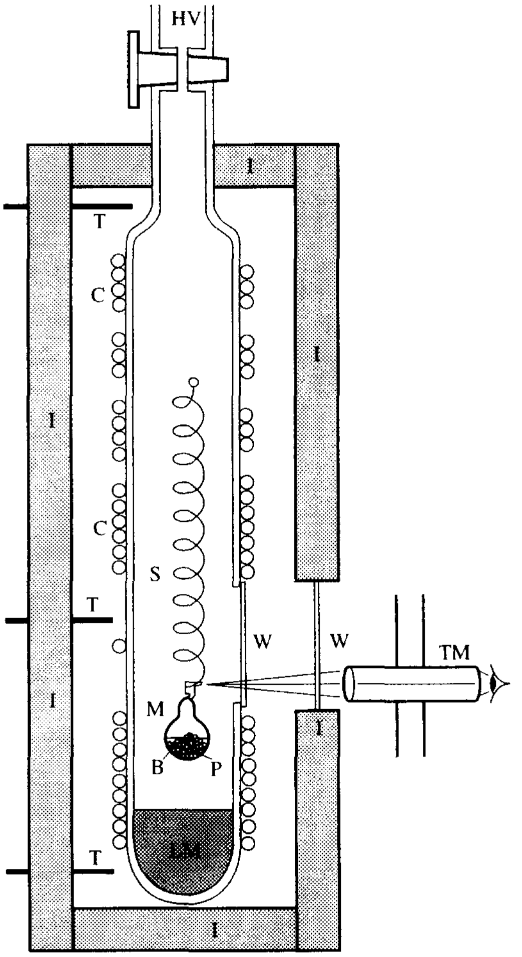

Figure 1 The arrangement of the popcorn, P, within a bucket, B, on a spring, S, that is suspended within a glass chamber containing the monomer vapour, M, showing how the length of the spring may be measured by viewing through the windows, W, with the travelling microscope, TM. Coils of copper tubing, C, circle the glass tube, GT, above and below the window, and provide temperature control, together with the polystyrene foam insulation, I. The reservoir of liquid monomer, LM, is at the bottom of the apparatus, and provides vapour at a partial pressure appropriate to the temperature of the system at the level of the bucket, about 10 cm above the monomer. The tube at the top leads through a tap to a high vacuum system, HV. The temperature of the air in the space enclosed within the insulation was monitored with thermometers, T. Joints in the glassware above and below the window section are not shown

45°C. Temperatures were controlled within this range by circulating water from a constant temperature bath through the copper coils about the glass vessel. The temperature of the air within the insulated enclosure was also controlled by this means. The spring of the balance was made of borosilicate glass filament about 0.5 mm thick, coiled in a helix about 10 mm across in 15 turns. Its length increased from about 3 cm to 5 cm when a mass of 1.0 g was placed in the bucket. Its extension, of 18.4 mm g^{-1}, was linear over this range to within the sensitivity of our length measurements (0.01 mm). The popcorn weights were thus accurate to about 2.5% at the start (typically 20 ± 0.5 mg) and to about 0.05% (typically 1000 ± 0.5 mg) at the end of a run.

Popcorn pieces about 10 to 20 mg in weight were cut expeditiously under a nitrogen blanket from a second or third generation sample that had grown at 20°C in liquid monomer for 2 days, and then had been stored in monomer for several weeks at −20°C until needed. A piece was transferred to the bucket through air, the apparatus was assembled, evacuated to a high vacuum, and then filled with white spot nitrogen that had been passed through a heated tube containing activated palladium catalyst (in a system supplied by Supelco) to remove any remaining oxygen and water. The monomer, which had previously been distilled and then purified by three or four freeze–pump–thaw cycles, was allowed to warm to the temperature of the experiment by passing water through the heating coils. The monomer developed a partial pressure appropriate to the temperature within the apparatus around the popcorn nodules.

Results and discussion

Popcorns were grown at nine temperatures within the range of 3°C to 40°C, the weight of the sample being measured at appropriate intervals using the spring balance. When the temperature was at the lower end of the range, measurements could be performed over a period of three days, but if the temperature was at the high end of the range, a maximum period of only 36 h was possible before the size of the popcorn became too large for the bucket. The samples grew from about 15 mg to about 1.0 g, that is by nearly two orders of magnitude. No seeding of new nuclei was observed, merely the growth of the nodules that we inserted. The weights are plotted against time on a logarithmic scale in *Figure 2*, the linearity of the plots over the final part of each growth process being a clear indication that the growth process is then first order, according to equation (1):

$$W_t = W_0 \exp(k_1 t) \qquad (1)$$

where W_t is the weight of the popcorn at time t, k_1 is the first-order rate constant and W_0 is the initial weight.

There may be seen to be induction periods of 2 to 10 h, depending upon the initial temperature. The existence of an induction period, during which the growth proceeds at a rate slower than the ultimate, is attributed to two main factors: the popcorn seed is primarily affected during the cutting process by the exposure to air, the oxygen of which is known to reduce the popcorn radicals' concentration[1]; and the temperature at which the growth was studied is different from that used to produce and store the seed. It was shown before that at 20°C the intensity of the radical e.p.r. signal grew relatively rapidly over a period of about 8 h by a factor of three before proceeding to grow at about the same rate as the popcorn itself[1]. The induction periods shown here in the plots of *Figure 2* undoubtedly have the same origin; they represent the time necessary for the growth process to become stabilized in a steady state. It is also possible that some time is needed for the popcorn to become permeated with monomer from the vapour phase. (The popcorn probably has densely crosslinked and highly strained nodules, within which the radicals multiply, surrounded by a more lightly crosslinked matrix[2,6], within which the monomer is initially absorbed.) The thermodynamic activity of the monomer within the popcorn is the same as if the popcorn were bathed directly with the liquid itself.

Once the plots become linear, it may be seen that the points lie very well on straight lines over several periods of weight doubling. From the slopes of these lines the values of the first-order rate constant, k_1, have been

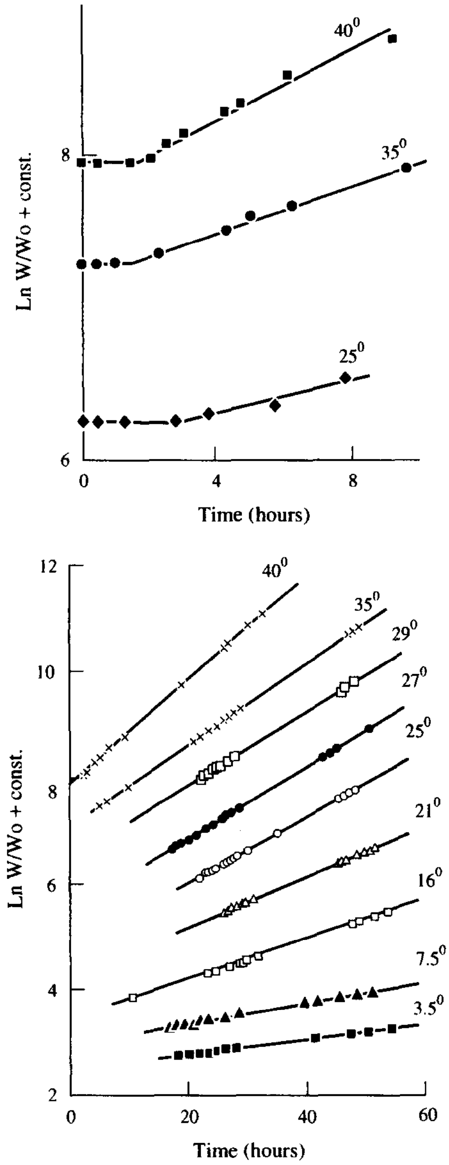

Figure 2 Plots of ln W_t/W_0 against time for popcorns grown within the McBain balance at the temperatures indicated at the ends of the lines. Each set of points has been raised above the set for the temperature immediately below by a constant to allow them to be clearly distinguished. (a) Measurements made during the initial period; (b) measurements made when the plots had become linear

obtained. By interpolation the value at 20°C may be estimated as $43.4 \times 10^{-3}\,h^{-1}$, which compares well with the value of $51 \times 10^{-3}\,h^{-1}$ estimated previously from the growth of the e.p.r. signal within a sealed tube. Weight measurements of popcorn growth and e.p.r. measurements on radical signals are in fair agreement.

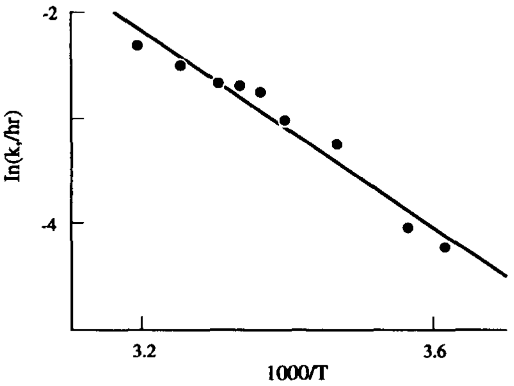

Figure 3 Arrhenius plots of first-order rate constants, k_1 from *Figure 2*, of popcorn growth against $1000/T$. The activation energy was found to be $38.4 \pm 0.7\,kJ\,mol^{-1}$

The Arrhenius plot of the rate constant data is shown in *Figure 3*, from which the slope provides an activation energy of $38.4(\pm 0.7)\,kJ\,mol^{-1}$. This value may be compared with that of $38\,kJ\,mol^{-1}$ obtained by observing the growth of the radical within popcorn with an e.p.r. instrument[1] and with the value of $40.7\,kJ\,mol^{-1}$ which has been obtained by measurements of the polymerization of the monomer within an emulsion system[7]. Our value for the Arrhenius A parameter is $2.96 \times 10^5\,h^{-1}$.

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