EXIT IN THE EMULSION POLYMERIZATION OF VINYL ACETATE

H.De Bruyn, R.G.Gilbert[*]
School of Chemistry, F11, University of Sydney, 2006, Australia

In most emulsion polymerizations the exhaustion of the separate monomer phase is followed by a decrease in conversion rate due to the decrease in monomer concentration in the latex particles. The unusual feature of vinyl acetate is that the rate remains constant throughout most of the period of decreasing monomer concentration.

There are two postulated mechanisms consistent with the observed kinetics.[1] Both require that $k_{ex} = k_{tr}C_p$ and this can be tested with a gamma radiolysis experiment.[2] (k_{ex} = exit rate coefficient, k_{tr} = rate coefficient for transfer to monomer and C_p = monomer concentration in particles).

An automatic tracking device (developed by David Sangster) measures the meniscus height in a dilatometer every three seconds. When the dilatometer is removed from the gamma source initiation by radiolysis stops allowing k_{ex} to be determined directly from the relaxation data.

One aspect of relaxation experiments which is often overlooked is the effect of the heat of reaction on the temperature of the reaction mixture.[3] It was found that the temperature increased by as much as two degrees when the dilatometer was placed in the γ-source and the polymerization recommenced. This means that on removal from the source the reaction temperature decreases, the reaction mixture contracts and if this contraction is not taken properly into account, it appears as more conversion than there actually is. In other words the relaxation appears to take much longer than it should and entirely spurious interpretations may result.

In order to compensate for this effect the temperature and contraction of the reaction mixture were monitored (out of source) while the temperature of the water-jacket was lowered through the range appropriate to the particular experiment. These data were used to construct a calibration curve which, together with a sensitive temperature probe in the dilatometer, was used to correct the conversion/time data obtained during the relaxation experiment.

The system relaxes very quickly at 50°C, within the 3 second reading interval and therefore too fast to measure with our experimental setup. This is to be expected as $k_{tr}C_p \approx 5$ s^{-1} giving an expected half life for the relaxation of 0.14 s. However at 2°C the half life is about 10 times greater and measurement was possible giving $k_{ex} = 0.4 \pm 0.1$ s^{-1} which is consistent with the product $k_{tr}C_p \approx 0.5$ s^{-1} at 2°C.[4,5]

References:
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