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Particle growth in butadiene emulsion polymerization, 2^{a)}

Gamma radiolysis

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SUMMARY:

The kinetics of the emulsion polymerization of butadiene at 60 °C in Smith-Ewart interval III were investigated using gamma radiation to produce initiating species. The aim of this work was to determine radical desorption rate coefficients through monitoring non-steady state kinetics. The acquired data of the average number of radicals per particle (\bar{n}) were in good agreement with data obtained from chemically initiated experiments. It was shown that the approach to steady state is kinetically determined and that thermal background initiation is negligible in the butadiene emulsion polymerization. While radical desorption rate coefficient data was determined with high uncertainty, the results are consistent with the transfer diffusion mechanism of radical exit.

Introduction

In an effort to elucidate the kinetic behaviour of the emulsion polymerization of butadiene, experiments were performed to monitor non-steady state kinetics. These can be observed in a system with the ability to stop and restart a polymerization. From the steady state conversion/time history an average number of radicals per particle, \bar{n} , can be determined if the propagation rate coefficient, k_p , is known¹⁾. The parameters that determine \bar{n} , such as the rate coefficient for entry of radicals into particles, ρ , and the rate coefficient for exit of radicals out of particles, k , can be determined by monitoring non-steady state kinetics, the data being interpreted, e. g. using the 'slope and intercept' method¹⁾. The accuracy with which an intercept can be determined is critical. Stopping and restarting the polymerization a number of times on a short time scale compared to the total reaction time offers an elegant method of acquiring more accurate data, since all other variables can be kept reasonably constant this way. The usual way to meet these preconditions in emulsion polymerization is the use of gamma rays for the initiation of polymerizations²⁾. One can simply remove a reactor vessel in or out of a gamma source to stop and restart the initiation of the polymerization.

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Furthermore, when the reactor is out of source, 'thermal background' initiation and retardation phenomena can be monitored, as is explained in detail elsewhere^{1,3,4}.

Theory

In a gamma-initiated experiment the reactor is exposed to a ⁶⁰Co source emitting high energy gamma rays. The gamma rays create radicals in the water phase as shown in Eqs. (1) to (4). The OH^{*} radical is the most important radical for polymerization. The important aqueous phase reactions are⁵:



The gamma radiolysis experiments were performed at the Nuclear Research Laboratories of the Commonwealth Scientific and Industrial Research Organisation at Lucas Heights, Sydney, Australia. The ⁶⁰Co gamma source used was moderately strong (2 krad · h⁻¹), and from its radiation level at the time of measurement an equivalent peroxodisulfate initiator concentration can be calculated using a so-called *G*-value^{2,5,6}. For the experiments performed, this leads to an equivalent peroxodisulfate concentration of: 0,27 · 10⁻³ mol · dm⁻³. This value is important for the comparison between values for \bar{n} and ρ from experiments using chemical initiator and gamma radiation. Gamma radiolysis is an important tool for investigating kinetics because, after removal from the source, the virtually instantaneous annihilation of OH^{*} and other radicals means that the resulting relaxation kinetics are sensitive to intra-particle radical loss events. The resulting quantitative and qualitative inferences are valid for systems utilizing conventional chemical initiators. That is for zero-one systems, gamma relaxation studies give information on exit and the fate of exited free radicals.

Experimental part

The recipes used in chemically initiated polymerization are described elsewhere⁷ and are adapted only to the volume of the gamma radiolysis reactor (23 mL). Dilatometry was used as a method of on-line conversion monitoring. For butadiene, a liquefied gas, a special stainless steel dilatometer was used. The reactor and dilatometer system is shown in Fig. 1.

The volume change caused by polymerization is measured by monitoring the movement of the piston of a gastight syringe which is connected to the reactor. This process is automated utilizing a Linear Variable Differential Transformer (LVDT) device. The syringe is pressurized with argon up to 10 bar to assure a constant pressure and to immobilize the piston for movements other than those caused by volume changes in the reaction mixture.

The set up had several drawbacks. The reactor is designed to fit in the reactor cavity of the gamma source and is therefore rather small (reactor volume = 23 mL). As a consequence the amounts used in the recipes are too small for accurate weighing and sampling. The volume to surface ratio is undesirably small. The temperature of the reactor could not be accurately controlled, since no heat control coupling between reactor and thermostatic bath existed.

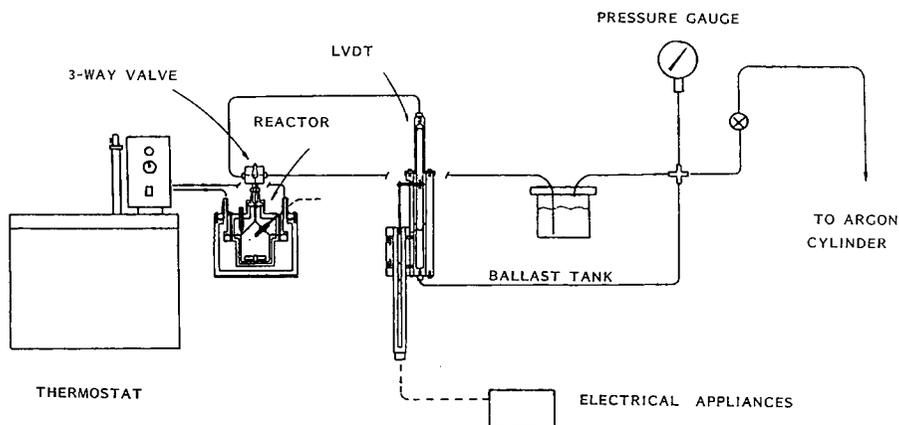


Fig. 1. The gamma radiolysis reactor and dilatometer system

Sampling during polymerization, necessary to convert the dilatometry data into conversion data, caused problems due to the small reactor volume. The sampling and subsequent gravimetric determination of the conversion are essential since butadiene and polybutadiene do not mix ideally, and therefore dilatometry, like densitometry, needs to be calibrated⁸⁾. The sampling is done by a gastight syringe, and the sample volume is replaced by water from the ballast tank. While taking a sample, the 3-way valve (see Fig. 2) is turned in such a way that the reactor is connected with the ballast tank and not with the LVDT. Sampling out of the reactor significantly reduces the amount of particles due to the small reactor volume as compared with the sample volume (1 mL). Therefore, after sampling, recalculation of the reactor contents is necessary, but this is only possible when the conversion at sampling time can be accurately determined. Errors introduced at the beginning of this procedure may have a large effect on the accuracy in the determination of the conversion of the last samples. Another problem arises from the fact that samples can only be taken while the reactor is out of the source and after decay, because sampling usually takes 5 to 10 min. Therefore, it was decided to take samples only three times during each polymerization: at the beginning of the reaction, after the first decay and after the second decay (3 data points are the minimal number required for a calibration curve!).

The gravimetric conversion determination indicated the limitations of the accuracy possible in the present design. The gravimetry measurement, accurate only to plus or minus 5% conversion, together with the errors in the weighing of the recipe ingredients, causes a relatively large inaccuracy in the data.

Results and discussion

Four gamma radiolysis experiments were performed. Conversion was determined with an error of about 5%, which means that also rates must have at least 5% error. Intercepts will have a much larger error. The most important data were taken from the steady state slope and intercept of polymerization during decay out of source, since the inhibition phenomena³⁾ should have no effect in this region. The most useful observation was the difference in approach to steady state between the first and the second insertion. The seeded recipes used begin the polymerizations at $w_p = 0.6$. This means, as was elucidated by Verdurmen et al.⁹⁾, that in plotting $-\ln(1 - x)$ versus time, two kinetic regions occur, the second of which is always linear. In Fig. 2 such a

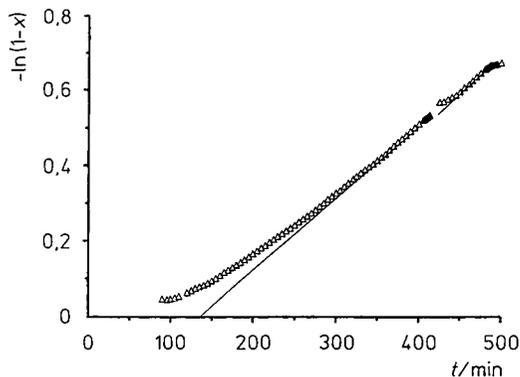


Fig. 2. $-\ln(1-x)$ versus time plot for a gamma radiolysis experiment consisting of two insertions in the gamma source (x = conversion)

plot is shown for a gamma radiolysis experiment. When the second linear region is reached, the second insertion in the gamma source leads to an approach to steady state that is purely kinetically determined. Fig. 2 proves the statements made by Verdurmen et al.⁹ that the non-linear regions observed in plots of $-\ln(1-x)$ versus time in interval III are not caused by inhibition effects nor by an approach to steady state over several hours, since the second approach to steady state is only determined by kinetics parameters and lasts only minutes.

The experiments were performed using 3 seed latexes of different particle sizes, the particle numbers were chosen so that the amount of polymer present in the system was constant. Either the first decay or the second decay was used to calculate the values for the average number of radicals per particle, \bar{n} , and the exit rate coefficient, k , listed in Tab. 1. The values of k were calculated assuming all exited free radicals in gamma relaxation undergo complete re-entry into particles, an assumption whose validity has been extensively verified for other monomers¹⁰⁻¹³. The \bar{n} values from chemically initiated systems (Verdurmen et al.⁷) using $k_p = 320 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ are presented for comparison. These \bar{n} values are obtained using exactly the same seed latexes but a peroxodisulfate concentration considerably higher than the calculated equivalent concentration created by the gamma source. This is acceptable due to the near independence of \bar{n} of the peroxodisulfate-initiated butadiene emulsion polymerization in the presence of tertiary dodecyl mercaptan (TDM)⁹. The equations used have been described elsewhere¹.

Note that the procedures used for chemically initiated polymerizations and gamma-initiated polymerizations were very different. The reactors used were different in shape and size, as was the way conversion was monitored and the initiating species. In this light the consistency between $\bar{n}_{SS}^{\text{chem}}$ and \bar{n}_{SS}^{γ} is a strong indication of the validity of the phenomenon that butadiene emulsion polymerizations in the presence of TDM are not affected by the peroxodisulfate concentration. Again this is an indication that TDM influences in-particle kinetics, as suggested by Verdurmen et al.⁹, since the water phase kinetics are totally different when comparing gamma radiolysis and peroxodisulfate initiation.

During the steady state reached when the reactor is out of source it is possible to measure the radical activity due to 'thermal background initiation' (in the absence of any other mechanism of initiation). The values of the entry rate coefficients (ρ^{decay})

Tab. 1. Calculated values for: the weight-average particle diameter, d_w , the particle number, N , the average number of radicals per particle, \bar{n}_{SS} (data from chemically initiated polymerizations: $\bar{n}_{SS}^{\text{chem}}$, gamma radiolysis: \bar{n}_{SS}^{γ} , reactor out of source: $\bar{n}_{SS}^{\text{decay}}$), and the exit rate coefficient, k

d_w nm	$10^{-19} \cdot N$ dm^{-3}	$\bar{n}_{SS}^{\text{chem}}$	\bar{n}_{SS}^{γ}	$\bar{n}_{SS}^{\text{decay}}$	k/s^{-1}
45	210	0,03 ^{a)}	0,05	0,002	0,3
90	29	0,2 ^{a)}	0,09	0,008	0,01
90 ^{b)}	29	—	0,04	0,02	0,02
150	6,7	0,3 ^{a)}	0,25	0,03	0,03

a) Values from Verdurmen et al.⁷⁾ experiments performed at $[\text{S}_2\text{O}_8^{2-}] = 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$.

b) Experiment performed without tertiary dodecyl mercaptan (TDM).

and the values of $\bar{n}_{SS}^{\text{decay}}$ depicted in Tab. 1 (calculated from the steady state reached when the reactor is out of source) are very low and comparable to the \bar{n} obtained from a thermal run performed: $\bar{n} = 0,012$ (Verdurmen et al.⁹⁾). This is a particularly useful result, since it indicates that 'thermal background initiation' is not an important source of radicals during decay. This leads to the reasonable assumption that 'thermal background initiation' is not important during gamma or chemically initiated polymerizations and need not be compensated when calculating initiator efficiencies.

Despite the high uncertainty in the values of k , some quantitative mechanistic inferences may be drawn from the data in Tab. 1. It has been shown¹¹⁻¹⁴⁾ that if all exited free radicals re-enter another particle and remain there without re-exiting, and if the exit process is governed by a transfer-diffusion mechanism, then the exit rate coefficient should vary as (swollen particle radius)⁻². The k -data of Tab. 1 can be fitted by (see Fig. 3):

$$k \approx (\text{swollen particle radius})^{-2,0 \pm 2,5}$$

While the exponent has a high uncertainty, the result is at least consistent with the transfer-diffusion mechanism for exit, with the fate of all exited free radicals being to re-enter another particle and remain there. This is the same behaviour as is shown by other studies on styrene¹¹⁻¹³⁾ and methyl methacrylate¹⁵⁾.

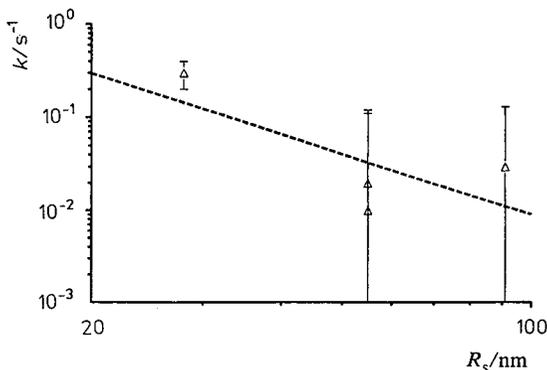


Fig. 3. The exit rate coefficient, k , as a function of swollen particle radius, R_s

Conclusions

The acquired \bar{n} data shows good agreement with chemically initiated data, even though different reactors, initiating species and concentration, and conversion monitoring systems were used. The data is in accord with the observation that \bar{n} is independent of the persulfate concentration and that TDM influences intra-particle kinetics. The reason for this behaviour remains unclear. It was shown that the approach to steady state in the seeded butadiene emulsion polymerization is kinetically determined and not caused by retardation phenomena. While the exit data is subject to high uncertainty, the results are consistent with the transfer-diffusion mechanism of radical exit, with desorbed free radicals re-entering particles and remaining there. Thermal background initiation can be neglected as an important source of radicals during gamma or chemically initiated polymerizations, as was deduced from the very low values for $\bar{n}_{SS}^{\text{decay}}$.

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