Thermochimica Acta, 72 (1984) 239–244
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

A CALORIMETRIC STUDY OF HETEROGENEOUS STYRENE POLYMERIZATION

H. BJÖRNBERG *, H. NILSSON and C. SILVEGREN
Dept. of Chem. Eng. II, University of Lund, P.O.B. 740, 220 07 Lund, Sweden
* Present address: Hoechst Perstorp AB, P.O.B. 5000, 284 00 Perstorp, Sweden

ABSTRACT

An isothermal 250 ml calorimetric reactor, especially designed to permit kinetic studies of radical polymerizations in heterogeneous systems is presented.

The calorimeter instantaneously measures the thermal power generated in the reactor autoclave. The power introduced by agitation is measured separately. The calorimeter can be used in the temperature range from 0 to 80 °C and at pressures up to 2 MPa. The resolution is about 10 mW.

The calorimeter was used to follow suspension and emulsion polymerizations of styrene at 60 °C. The heat of polymerization and the termination and propagation rate constants were evaluated. The viscosity dependent variation of the termination rate constant followed the predictions of the WLF equation over a considerable conversion range. A viscosity dependent decrease of the propagation was observed at high conversions.

INTRODUCTION

The free radical polymerization of styrene is probably the most frequently studied polymerization process. Despite this, many important aspects of styrene polymerization, such as the variation of individual rate constants with conversion and the transport of monomer and radicals within and between phases, are still unadequately known. One reason for this is the lack of rate data of high accuracy. In most previous studies, the polymerization has been followed by methods which measure the conversion. Such methods give rate data of rather low precision, especially when applied to heterogeneous polymerization systems. Previous work in this laboratory has indicated that calorimetry can be used as a convenient tool for obtaining kinetic data of good accuracy on such systems. A major advantage of calorimetry is that it measures a quantity, the power evolved in the polymerization process, which is directly proportional to the rate. In this paper the use of a newly designed calorimetric reactor system in the study of emulsion and suspension polymerization of styrene is demonstrated. It is shown that the results can provide information about the variations in the termination and propagation rate constants,

THE CALORIMETER

The calorimeter system was a slightly improved version of a system recently described in greater detail (ref. 1,2). The reactor vessel is shown in Fig. 1. When used, the reactor was immersed in a thermostated water bath, which served as a thermal reference. The bottom of the reactor was supplied with Peltier coolers. The temperature inside the reactor was measured by a thermistor. The thermistor signal was fed to a PID controller, which controlled the current to the Peltier coolers. By this technique the reactor temperature was maintained at the set point.

To measure the mechanical power evolved inside the reactor during the polymerization a torque transducer was mounted on the stirrer shaft below the packing gland.

For the purpose of theoretical modelling, the reactor system was assumed to consist of five different parts (ref. 2). These were the reference bath (R), the autoclave (A), the bottom flange (F) and the Peltier cooler, mathematically treated as one cold side (P') and one warm (P").

Each of these parts was assumed to have a homogeneous temperature, $\Theta_0 + \Theta_k$, where Θ_0 is the absolute set point temperature of the reference. Heat transfer between two parts of the reactor in thermal contact was described by a total heat transfer coefficient, $K_{k,l}$ (W/K), where k and l refer to the two parts in contact. The heat capacities were considered only for the autoclave with its content (C_A) and for the cold side of the Peltier coolers ($C_{P'}$). As has been shown in earlier work, such a simple model is quite satisfactory for polymerization studies.

From heat flow balance equations for the different parts of the theoretical model the following equation for the thermal power (P_A) evolved inside the reactor can be derived (ref. 2):

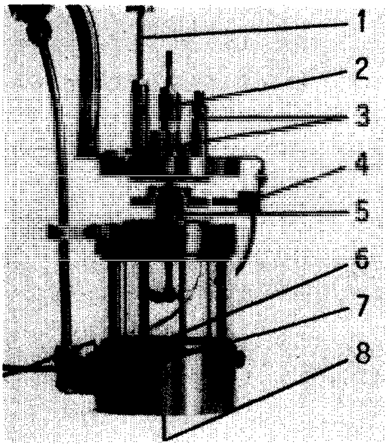

Fig. 1. The calorimeter reactor

1. Valve.
2. Packing gland.
3. Membrane fittings.
4. Pick up coil.
5. Torque transducer.
6. Thermistor (pulled half way out).
7. Reactor bottom flange.
8. Peltier elements.

$$P_A = \alpha \cdot i \cdot (\Theta_o + \Theta_{P'}) - (R/2) \cdot i^2 - K_{F,R}(\Theta_R - \Theta_R)$$
$$- K_{P',P''}(\Theta_{P''} - \Theta_{P'}) - K_{P'',F}(\Theta_{P''} - \Theta_F) + C_A(d\Theta_A/dt) + C_{P'}(d\Theta_{P'}/dt) \quad (1)$$

where α is the thermoelectric force coefficient, i is the current to the Peltier coolers and R is the electrical resistance of the Peltier coolers. The temperature Θ_R was assumed to be zero. To obtain P_A from Eq. 1 the current to the Peltier coolers (i), and the temperatures Θ_F, $\Theta_{P'}$ and $\Theta_{P''}$ were recorded. The temperature Θ_A was calculated from the current to the Peltier coolers. All other parameters in Eq. (1) were independent of the experimental conditions and were determined by calibration.

EVALUATION OF THE EXPERIMENTAL KINETIC DATA

The heat evolved by chemical reactions, P_{Chem}, was evaluated from the following expression:

$$P_A = P_{Chem} + P_{agitation}$$

The thermal power associated with phase transitions was neglected in the present experiments. Calculations using literature data showed that this could be safely done.

In polymerization systems where polymers of high molecular weight are formed the propagation reaction dominates completely over all other reactions and is thus the only one considered in the power balance equation. The rate of polymerization is given by

$$r_P = - P_{Chem}/\Delta H_P \quad (2)$$

The total mass balance of styrene was calculated as the sum of polystyrene, obtained by integrating eq.(2), styrene dissolved in the polymer phase and free, liquid styrene. The contents of styrene in the vapour and aqueous phase were neglected. Materials, except monomer, and procedures were similar to those described earlier (ref. 2).

THEORY

The kinetic expression for suspension polymerization of styrene is given by

$$r_P = k_p \cdot [M] \cdot (f \cdot k_d \cdot [I] \ /k_t)^{1/2} \quad (3)$$

where k_p is the propagation rate constant, [M] the monomer concentration in the monomer/polymer phase, k_d the decomposition rate constant for the initiator, [I] is the initiator concentration, k_t the termination rate constant and f the efficiency factor for the initiator.

As the polymerization proceeds the polymerizing phase becomes more and more viscous which leads to a decrease in the diffusivity of the polymer radicals and consequently to a decrease of the rate of termination.

If it is assumed that the diffusivities could be expressed by the WLF equation and that the rate constants are proportional to the diffusion constants, the logarithms of the rate constants would be proportional to the inverse of the free volume of the monomer/polymer phase. The free volumes were estimated from the volume fractions and glass transition temperatures of styrene and polystyrene as suggested by Hamielec (ref. 3).

The rate expression for emulsion polymerization is given by

$$r_P = k_p \cdot [M] \cdot \bar{n} \cdot N/N_A \qquad (4)$$

where $\bar{n}$ is the average number of radicals per particle, N is the total number of particles and N_A is Avogadro's number.

An emulsion polymerization is usually divided into three intervals, I-III. In interval I polymer particles are formed. The total number of particles increases until interval II is reached. In this interval N is constant and monomer is transported from the monomer phase to the particles where it polymerizes. In this interval the monomer concentration in the particles is high and rather constant. The viscosity is low. If radicals do not leave the particles and if the termination rate is high compared to the rate of entrance of radicals into the particles, each particle will contain either one or no radical i.e. on the average 0.5 radicals per particle. The monomer concentration in the particles is determined by the balance between the interfacial tension and the tendency to swell due to osmotic forces. Interval III starts when the free monomer phase has disappeared. In this interval the monomer concentration in the particles decreases.

RESULTS AND DISCUSSIONS

The termination rate constant, k_t, from different suspension polymerization experiments was calculated according to eq. (3). In the calculations of k_t all variations in the other rate constants will be included. The composition in the polymerizing phase was obtained from the conversion curve. Fig. 2 presents data of the logarithm of k_t versus the inverse of the free volume for two different polymerization experiments with azobisisobutyronitrile as initiator. The decrease in the logarithm of k_t versus the inverse of the free volume is almost linear in accordance with the WLF theory. It should reach a low limiting value at the glass transition composition.

The constant k_p value used in the calculation of k_t was obtained from emulsion polymerization experiments using eq. (4) assuming $\bar{n}$ to be 0.5. In separate experiments it was shown that extra addition of initiator during interval II

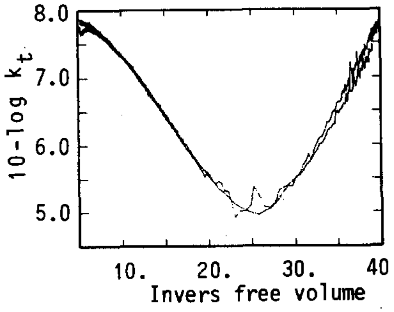

Fig. 2. The 10-logarithm of the termination rate constant versus the inverse free volume as calculated by eq. (3).

did not affect the rate of polymerization. This strongly indicates that $\bar{n}$ was 0.5. The apparent decrease in k_t at inverse free volumes greater than 26.3 depends on the fact that k_p, k_d and possibly f have been influenced by the increasing viscosity of the polymerizing phase. A similar experiment using dilauroyl peroxide instead of azobisisobutyronitrile as initiator showed the same characteristics in k_t, but only at inverse free volumes lower than 25. At large values of the inverse free volume the slope was different. This implies that different initiators exhibit different behaviour in highly viscous media, The same phenomenon has been found for vinyl chloride polymerization (ref. 2). Fig. 3 shows the results from three different emulsion polymerizations.

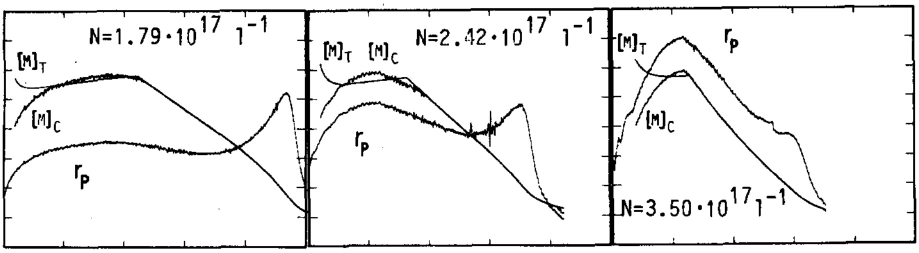

Fig. 3. Emulsion polymerization experiments. The graphs represent rate of polymerization (r_p), calculated and theoretical styrene concentrations ($[M]_C$ and $[M]_T$ resp.) versus time. All units are arbitrary.

From eq. (4) it is obvious that the rate of polymerization can not decrease except because of a decrease in the monomer concentration. Assuming $\bar{n}$ to be 0.5 and using a k_p value of 205 (l/mol·s) the corresponding value of the styrene concentration, $[M]_C$, was calculated. The results are shown in Fig. 3 and agree fairly well with the styrene concentration, $[M]_T$, as calculated from theories (ref. 4). The difference between $[M]_C$ and $[M]_T$ might be due to diffusion controlled monomer transport.

The free volume dependence of k_p can not be evaluated from the data shown in Fig. 2 since these reflect the behaviour of several parameters. The maximum and minimum variation in k_p during interval III can be estimated by using the largest and smallest values of $\bar{n}$ possible. Since $\bar{n}$ can not decrease in interval II

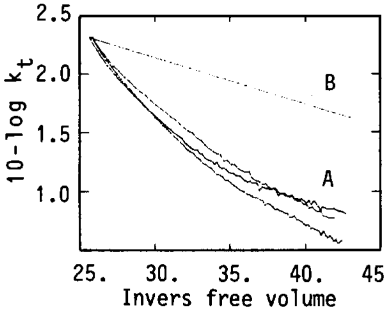

Fig. 4. The propagation rate constant calculated for the three emulsion polymerizations shown in Fig. 3, assuming $\bar{n}$ to have its theoretically largest and smallest values (Curves A and B, respectively).

the smallest value is 0.5. The largest value can be calculated assuming no termination at all, i.e. all produced radicals are accumulated in the particles. The results of these calculations are presented in Fig. 4.

The heat of polymerization, evaluated from the polymerization experiments in this work, was found to be 75 ± 2 kJ/mol.

REFERENCES

1 H. Nilsson, C. Silvegren and B. Törnell, Chem. Scr., 19 (1982) 164.

2 H. Nilsson, C. Silvegren and B. Törnell, Ang. Macromol. Chem., 112 (1983) 125.

3 A.E. Hamielec, R. Gomez-Vaillard and F.L. Marten, J. Macromol. Sci.-Chem., A17 (6), (1982) 1005.

4 C.M. Tseng, M.S. El-Asser and J.W. Vanderhof, Computer Application in Applied Polymer Science (Ed. T. Provden), ACS Symp. Ser. 197, Washington, DC (1982).